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CONTENTS OF VOLUME 57

NUMBER 1

Cementation of Some California Tertiary Reservoir Sands. Charles M. Gilbert . . 1

The Facies Classification of Rocks: A Clue to the Origin of Quartzo-Feldspathic Massifs and Veins. Hans Ramberg 18

Frequency Distribution of the Minerals in Two Petrographic Provinces. Tom. F. W. Barth 55

Oxidation and Reduction in Geochemistry. Brian Mason 62

Cellular Structures in Glass as Related to Structures in Lava. E. F. Osborn . . 73

Geological Notes

Naturally Briquetted Coal from a Bed in Western Pennsylvania. James M. Schopf 79

Stylolites in Pre-Cambrian Quartzite. C. E. B. Conybeare 83

Recent Shoreline Changes at Shirley Gut, Boston Harbor. Robert L. Nichols . 85

Rocks of the Mid-Atlantic Ridge. S. J. Shand 89

Discussion

Radial Diffusion and Chemical Stability in the Gravitational Field: A Discussion. Jean Verhoogen 93

Radial Diffusion and Chemical Stability in the Gravitational Field: A Reply. Hans Ramberg 95

Reviews

"The Geological Approach to the Study of Soils," W. H. Bryan (C. A. Cotton) . . . 98

Sequence in Layered Rocks, Robert R. Shrock (N. A. R.) 99

Chambers's Minerological Dictionary (D. J. F.) 99

Communications and Announcements 100

NUMBER 2

The Geologic Implications of Cryopedology. Kirk Bryan 101

Oriented Lakes of Northern Alaska. Robert F. Black and William L. Barksdale . . 105

Thaw Lakes and Thaw Sinks in the Imuruk Lake Area, Seward Peninsula, Alaska. David M. Hopkins 119

A Possible Fossil Ice Wedge in Bureau County, Illinois. Leland Horberg 132

Rock-Fragment Slopes Caused by Past Frost Action in the Jura Mountains (Ain), France. Sheldon Judson 137

Stone Nets, Stone Stripes, and Soil Stripes in the Wind River Mountains, Wyoming. Gerald M. Richmond 143

Some Periglacial Features in Central Montana. J. P. Schafer 154

Pleistocene Ventifacts East of the Big Horn Mountains, Wyoming. Robert P. Sharp 175

Periglacial Features in the Driftless Area of Southern Wisconsin. H. T. U. Smith 196

The Frost-Moved Rubbles of Jumbo Dome and Their Significance in the Pleistocene Chronology of Alaska. Clyde Wahrhaftig 216

Reviews

"Strukturböden, Solifluktion und Frostklimate der Erde," Carl Troll (Ernst Antevs) 232

"Die morphologischen Wirkungen des Eiszeitklimas im gletscherfreien Gebiet," Julius Büdel (Ernst Antevs) 235

Études de cryopédologie, André Cailleux (L. H.) 236

"Landscape Study in South Africa," Lester C. King (C. A. Cotton) 236

Climatic Accidents in Landscape Making, C. A. Cotton (L. H.) 238

NUMBER 3

On Ratio Correlation in Petrography. F. Chayes 239

Some Examples of the Application of Thermochemistry to Petrology. Th. G. Sahama and D. R. Torgeson 255

Isostasy—Extended. Ross Gunn 263

A Review of Tectonic Relief in Australia. C. A. Cotton 280

Leaching of Carbonates in Glacial Drift and Loess as a Basis for Age Correlation. Richard Foster Flint 297

Geological Notes

Liquid Inclusions in Granite Thermometry. Sturges W. Bailey 304

Source Area of Great Plains Pleistocene Volcanic Ash. Ada Swineford . . . 307

Discussion

Crustal Movement in the Great Lakes Area: A Discussion. William Herbert Hobbs 312

Ancient Arctica: Remarks and Supplement. Wolf Mayne 314

Ancient Arctica: Reply to Remarks. A. J. Eardley 319

Reviews

Geological Map of the Province of Ontario: Map. No. 1946-3, J. Satterly (F. J. P.) . . 321

Geological Map of Saskatchewan, Map 895A (H. S. Armstrong) 321

Mineral Map of Saskatchewan, Map 896A (H. S. Armstrong) 323

Geological Map of Manitoba, Map 850A (H. S. Armstrong) 323

The Ancient Volcanoes of Oregon, Howel Williams (F. M. Byers, Jr.) 324

Gesteine und Minerallagerstätten, vol. 1, P. Niggli (T. F. W. B.) 325

Geological Explorations in Western Tibet, E. Norin (T. F. W. B.) 326

Festschrift Paul Niggli, zu seinen 60. Geburtstag (T. F. W. B.) 326

Technische Gesteinskunde, A. von Moos and F. de Quervain (R. B.) 327

The "Stratigraph" (R. B.) 327

Heat Conduction, with Engineering and Geological Applications, L. R. INGERSOLL, O. J. ZOBEL, AND A. C. INGERSOLL (T. S. Lovering) 327

COMMUNICATIONS AND ANNOUNCEMENTS 330

NUMBER 4

STRUCTURAL PETROLOGY OF PLANES OF LIQUID INCLUSIONS. O. F. Tuttle 331

ON THE GRANITE PROBLEM. R. Perrin and M. Roubault 357

VILLAFRANCHIAN STRATIGRAPHY IN SOUTHERN AND SOUTHWESTERN EUROPE. Hallam L. Movius, Jr. 380

GEOLOGICAL NOTES

SOME REMARKABLE WIND-FACETED PEBBLES FROM NEAR THE MOUTH OF THE UMHLANGAKULU RIVER, SOUTHERN NATAL, SOUTH AFRICA. Lester King 413

GEOCHEMICAL RESEARCHES IN JAPAN. Kazuo Yamasaki 414

A FLORIDA LANDSLIDE. Richard H. Jordan 418

DISCUSSION

THE DISTRIBUTION OF OXYGEN IN THE LITHOSPHERE AND OXYGEN IN ROCKS: A BASIS FOR PETROGRAPHIC CALCULATIONS: A DISCUSSION. Ivan Th. Rosenqvist 420

THE DISTRIBUTION OF OXYGEN IN THE LITHOSPHERE: A REPLY. Tom. F. W. Barth . . 423

THE DISTRIBUTION OF OXYGEN IN THE LITHOSPHERE: COMMENTS ON BARTH'S REPLY. Ivan Th. Rosenqvist 425

THE USE OF OXYGEN AS A REFERENCE SUBSTANCE IN PETROGRAPHIC CALCULATIONS: A SUPPLEMENT AND A REPLY. Tom. F. W. Barth 425

THE PRESERVATION OF ANTARCTIC ICE SPECIMENS: A DISCUSSION. Henri Bader . . . 427

THE PRESERVATION OF ANTARCTIC ICE SPECIMENS: A REPLY. Arthur David Howard . 428

ALBITE-WATER SYSTEM IN THE GRAVITATIONAL FIELD: A COMMENT. Hans Ramberg . 429

REVIEWS 432

COMMUNICATIONS AND ANNOUNCEMENTS 443

ERRATUM 443

NUMBER 5

CARLSBAD CAVERNS AND OTHER CAVES OF THE GUADALUPE BLOCK, NEW MEXICO. J Harlen Bretz 447

GEOMORPHIC HISTORY OF THE CARLSBAD CAVERNS AREA, NEW MEXICO. Leland Horberg . 464

THE OGALLALA FORMATION WEST OF THE LLANO ESTACADO. J Harlen Bretz and Leland Horberg 477

CALICHE IN SOUTHEASTERN NEW MEXICO. J Harlen Bretz and Leland Horberg 491

TOPOGRAPHY AND SEDIMENTS OF THE ARCTIC BASIN. K. O. Emery 512

REPLACEMENT AND THE EQUATING OF VOLUME AND WEIGHT. John Ridge 522

REVIEWS

"Die Metamorphose der Kohle und ihr Einfluss auf die sichtbaren derselben," W. PETRASCHECK (G. H. Cady) 551

NUMBER 6

PETROGENESIS OF PERTHITE PEGMATITES IN THE BLACK HILLS, SOUTH DAKOTA. Riad A. Higazy 555

SANDSTONE TYPES: THEIR ABUNDANCE AND CEMENTING AGENTS. Sefton L. Tallman . . . 582

RECENT RESULTS OF INVESTIGATIONS ON THE FELDSPARS. Alexander Köhler 592

DIE HÄUFIGKEIT DER EDELGASE AUF DER ERDE UND IM KOSMOS. Hans E. Suess 600

A NOTE ON THE GEOCHEMISTRY OF THALLIUM. Kalervo Rankama 608

GEOLOGICAL NOTES

TRIVOLI SANDSTONE OF WILLIAMSON COUNTY, ILLINOIS. Raymond Siever 614

A PROPOSED METHOD FOR THE MEASUREMENT OF GEOLOGIC TEMPERATURES. I. I. Friedman 618

REVIEWS

Cretaceous and Tertiary Subsurface Geology: The Stratigraphy, Paleontology, and Sedimentology of Three Deep Test Wells on the Eastern Shore of Maryland (W. C. Krumbein) 620

"Boden- und Klimaverhältnisse in Mittel- und Westeuropa während der Würmeiszeit," HANS POSER (Ernst Antevs) 621

Soil Mechanics in Engineering Practice, KARL TERZAGHI and RALPH B. PECK (Parker D. Trask) 622

Physical Geology, CHESTER R. LONGWELL, ADOLPH KNOPF, and RICHARD FOSTER FLINT (Lou Williams Page) 623

The Religion of the Modern Scientist (Neo-materialism), S. W. TROMP (Kirtley F. Mather) 625

Mining Geology, H. E. MCKINSTRY, with sections by STANLEY A. TYLER, E. N. PENNEBAKER, and KENYON E. RICHARD (Olaf N. Rove) 625

The Iron Resources of California (Charles F. Park, Jr.) 626

COMMUNICATIONS AND ANNOUNCEMENTS 628

ERRATA 628

INDEX 629

SCIENCE AND INDUSTRY

THE JOURNAL OF GEOLOGY

STACKS
REFERENCE
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VOLUME 57 JANUARY 1949 NUMBER 1

CEMENTATION OF SOME CALIFORNIA TERTIARY RESERVOIR SANDS
Charles M. Gilbert 1

THE FACIES CLASSIFICATION OF ROCKS: A CLUE TO THE ORIGIN OF QUARTZO-FELDSPATHIC MASSIFS AND VEINS . . . . . Hans Ramberg 18

FREQUENCY DISTRIBUTION OF THE MINERALS IN TWO PETROGRAPHIC PROVINCES
Tom. F. W. Barth 55

OXIDATION AND REDUCTION IN GEOCHEMISTRY . . . . . Brian Mason 62

CELLULAR STRUCTURES IN GLASS AS RELATED TO STRUCTURES IN LAVA
E. F. Osborn 73

GEOLOGICAL NOTES
Naturally Briquetted Coal from a Bed in Western Pennsylvania . James M. Schopf 79
Stylolites in Pre-Cambrian Quartzite . . . . . C. E. B. Conybeare 83
Recent Shoreline Changes at Shirley Gut, Boston Harbor . . . Robert L. Nichols 85
Rocks of the Mid-Atlantic Ridge . . . . . S. J. Shand 89

DISCUSSION
Radial Diffusion and Chemical Stability in the Gravitational Field: A Discussion
Jean Verhoogen 93
Radial Diffusion and Chemical Stability in the Gravitational Field: A Reply
Hans Ramberg 95

REVIEWS
"The Geological Approach to the Study of Soils," W. H. Bryan (C. A. Cotton) 98
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Chambers's Mineralogical Dictionary (D. J. F.) 99

COMMUNICATIONS AND ANNOUNCEMENTS 100

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IN KEEPING with our policy of reserving an occasional issue of the *Journal* for some rapidly advancing field of research, an early number will be devoted to periglacial and permafrost phenomena. Study of the geology of polar regions, especially the problems of permafrost, was greatly accelerated by war research in the Arctic. It seems appropriate, therefore, to devote an issue of the *Journal* to the science of permafrost.

Although periglacial and permafrost features are confined principally to the polar regions today, they are widespread, though commonly overlooked, in and near the areas glaciated during the Pleistocene. Papers which deal with "fossil" frost and periglacial structures will be included, therefore, in our permafrost number.

Unlike the papers of many symposia which review past achievements, the papers in the forthcoming issue of the *Journal* will present only new material.

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TEXT—Manuscripts should be written in English, or in French or German with an adequate summary in English. They should be typewritten, on one side of paper only, double spaced, and with wide margins.

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——— (1884*b*) Guidebook for excursions in the Big Ben Mountains, New York, Macmillan Co.

SMITH, A. V. (1926) Discovery of fish remains in Ordovician rocks of the Black Hills (abstr.): Geol. Soc. America Bull. 52, p. 27.

——— and DUNSANY, A. J. (1929*a*) Early Ordovician faunas of South Dakota: U.S. Geol. Survey Bull. 444, pp. 1–76, 3 pls.

——— — ——— (1929*b*) Revision of Ordovician stratigraphy of the Black Hills: Jour. Geology, vol. 37, pp. 680–695.

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VOLUME 57 NUMBER 1

THE JOURNAL OF GEOLOGY

January 1949

CEMENTATION OF SOME CALIFORNIA TERTIARY RESERVOIR SANDS[1]

CHARLES M. GILBERT
University of California, Berkeley, California

ABSTRACT

Forty core samples of feldspathic sandstones from wells in central and southern California contain the following secondary (authigenic) minerals deposited in the open pores or formed within the detrital clay matrix: quartz, albite, orthoclase, microcline, dolomite, calcite, anatase, kaolinite (?), glauconite, barite, and pyrite. These minerals, together with the primary clay matrix prominent in some samples, are the cementing substances.

Secondary quartz occurs as crystallographically continuous outgrowths on detrital grains. The secondary feldspars are both outgrowths on detrital feldspars and idiomorphic authigenic crystals in cavities. Dolomite takes the form of small rhombs and is most abundant in the clay matrix, whereas calcite is typically an anhedral cement filling open pores. Kaolinite (?) occurs as radial fibrous or granular aggregates in the detrital clay matrix. Dolomite and secondary feldspars have idiomorphic outlines in contact with secondary quartz and calcite, and in many cases calcite has grown on top of secondary idiomorphic quartz.

Intricately penetrating contacts between detrital grains of quartz and feldspar may be the result of grain-on-grain pressure and consequent solution at points of contact between grains. The crystallization of secondary quartz and feldspar may be complementary to such local solution.

INTRODUCTION

This paper reports the first results of an investigation of the characteristics and sequence of deposition of cementing materials and the resulting rock texture in some California Tertiary reservoir sandstones. The results of somewhat similar but more extensive study of Rocky Mountain sandstones made by W. A. Waldschmidt (1941) led the writer to undertake an examination of cements in California sandstones.

This study was limited to forty core samples from four wells of the Standard Oil Company in central and southern California. The samples studied (ten from each of the four wells) represent small stratigraphic intervals in each of the wells, as follows (see also table 2):

Well A.—Pleasant Valley Field, Fresno County, California. The samples from this well are numbered S3-1A to 10A and were taken from depths between 9,069 and 9,142 feet, representing the Gatchell sand of Middle Eocene age.

Well B.—Coalinga Extension Field, Fresno County, California. Samples from this well are S3-1B to 10B, were taken from depths between 8,172 and 8,230 feet, and represent the Gatchell sand of Middle Eocene age.

Well C.—Kettleman Middle Dome, Kings County, California. Samples from this well are numbered S3-1C to 10C,

[1] Manuscript received July 12, 1948.

were taken from depths between 12,195 and 12,240 feet, and represent the McAdams sand of Middle Eocene age.

Well F.—Los Angeles Basin north of West Coyote Field, Los Angeles County, California. Samples from this well are numbered S3-1F to 10F, were taken from depths between 10,358 and 10,805 feet, and represent the Puente sandstone of Upper Miocene age.

Thin sections of each sample mounted on a universal stage were investigated by techniques developed during the course of this study but described elsewhere (Gilbert and Turner, 1948). The universal stage proved invaluable and is recommended for sedimentary petrographic examinations, especially for detailed studies of textures and authigenic minerals in thin sections or permanent grain mounts.

The samples were small cores approximately 1 inch in diameter, embedded in wax, on which permeability measurements had been made. The orientation of the cores with respect to the bedding is unknown, but thin sections cut across these cores must be inclined at a considerable angle to the bedding because the thin dimension of the mica flakes was invariably seen in section.

Two of the three formations studied, the Gatchell and McAdams sands, productive zones of Eocene age, are described from the subsurface in the Kettleman Hills–Coalinga area but are not recognized in surface outcrops. They are generally rather well-sorted, permeable, medium-grained sandstones reaching a thickness of several hundred feet in some places but typically lensing so that they form a type of stratigraphic trap. The Puente formation is a thick series of shales and sandstones of Upper Miocene age cropping out in the northern part of the Los Angeles Basin. Although the formation is mostly shale, considerable sandstone occurs in its middle and upper part. In the cores examined, the Puente sandstone, unlike the better-sorted Gatchell and McAdams sands, is characterized by a clay matrix.

MINERALOGY OF THE SANDSTONES

DETRITAL MINERALS

All the sandstones are light colored and feldspathic. Those from wells A, B, and C (Gatchell and McAdams sands) contain on the average approximately 65–70 per cent quartz and 30–35 per cent feldspar most of which is orthoclase or microcline; the Puente sandstone from well F is more feldspathic, containing at least 50 per cent feldspar of which about half is plagioclase. Clay is abundant in some samples but is lacking in others. Detrital heavy minerals make up approximately 1 per cent of the sandstones; they include zircon, tourmaline, garnet, apatite, and sphene with minor amounts of hypersthene, augite, and hornblende. Solution etching appears on grains of garnet, hypersthene, and augite.

SECONDARY MINERALS

Minerals that have crystallized in the sands after their deposition are classed collectively as secondary or authigenic. In the sandstones examined such minerals include quartz, orthoclase, microcline, albite, dolomite, calcite, kaolinite(?), glauconite, anatase, barite, and pyrite. They may have been formed by processes operating at the time of deposition or by chemical activity of connate waters following deep burial. The writer believes the latter origin to be more probable. Possibly some of the secondary minerals crystallized under the influence of regional stress or circulating ground waters of surface origin, but there is no

reason to suspect that any of them is the direct product of surface weathering or of igneous hydrothermal emanations.

Classified according to type of cement, the samples may be divided into two groups—one in which the cement is chiefly a clay matrix and another in which chemically precipitated secondary minerals are the chief binding material. Such a subdivision probably could be applied to any extensive suite of sandstones (Waldschmidt, 1941, p. 1857; Krynine, 1948, p. 138). Very fine detrital material, called clay although its specific components are not determinable, fills the spaces between sand grains in many of the samples and by compaction and partial recrystallization to kaolinite has become coherent, forming a cement. Sandstones cemented chiefly by clay include some in which detrital clay and recrystallized kaolinite are the only binding materials and others in which rhombohedrons of dolomite occur throughout the clay and here and there fill the spaces between sand grains. In such rocks calcite and secondary quartz and feldspars are absent or occur in minor amounts—a fact suggesting that the clay has inhibited the normal precipitation of secondary minerals in open pores.

Where detrital clay is lacking or present in only small amounts, chemically precipitated secondary minerals are typically more abundant. In a few samples calcite fills the spaces between sand grains and is the chief cement; in others the cement is secondary quartz, commonly accompanied by less abundant secondary feldspars; and in some quartz, feldspar, and calcite all combine to bind the sand grains together.

Quartz.—Secondary quartz in the form of crystallographically continuous outgrowths on detrital grains is present in every sample from wells A and C and as smaller outgrowths in most of the samples from wells B and F. Where a prominent detrital clay matrix is present, quartz outgrowths are either small or lacking altogether. In samples from wells A and C secondary quartz is the chief cement, but all of it occurs as enlargements of detrital grains, and none in the form of granular aggregates between detrital grains has been found.

Evidence of quartz enlargement is of several kinds. Most convincing are the perfect crystal forms projecting into partly filled cavities. The faces formed cannot always be seen unless the thin section is tilted on a universal stage (Gilbert and Turner, 1948). Even a slight tilt may bring into sharp focus crystal faces which might otherwise be obscure or overlooked entirely. Faces are evident on many of the grains when they are disaggregated and examined with a binocular, but under these circumstances the textural relations are not evident. Some outgrowths can be recognized in thin sections and distinguished from the detrital portion of the quartz by the presence of a dusty line or zone of inclusions representing the original surface of the detrital grain. But in the sandstones studied many, if not most, of the angular detrital grains were originally bounded by clean surfaces so that the contact with the quartz overgrowth may be obscure or invisible. Where the idiomorphic form of the quartz outgrowth, together with a dusty line representing the original surface of the detrital grain is seen, both the existence and the size of the outgrowths are established. The sandstones most tightly cemented by secondary quartz have an interlocking texture in which the added quartz has completely filled much of the original pore space and is molded by the adjacent grains. In such rocks, idiomorphic forms are lacking and the inti-

mately interlocking grain contacts alone are evidence of quartz outgrowth.

Measurements made with a universal stage (Gilbert and Turner, 1948) on many idiomorphic outgrowths show that the faces developed belong to the most common crystal forms of quartz, that is, the unit prism and the positive and negative unit rhombohedrons—{10$\bar{1}$0}, {10$\bar{1}$1}, {01$\bar{1}$1}. All three of these forms are represented on the large outgrowth seen on the central quartz grain of plate 4, *E* and figure 4. Among all the faces determined, a single pyramid, {11$\bar{2}$1}, was found on one crystal. This may mean that only the more common forms tend to develop, or it may be that other faces are smaller and cut only rarely by the thin section.

In a number of cases quartz enlargements have been observed on as many as three or four detrital grains surrounding the same void, so that apparently the outgrowths are not added in any one favored direction in the fabric. Where outgrowths from two sides of a cavity have made contact, the bounding surfaces between them commonly appear to be planes, but in no case have they proved to be rational crystal faces of either quartz grain.

Feldspar.—Secondary feldspar includes orthoclase, microcline, and albite and is not nearly so abundant as secondary quartz. However, it has been observed in every sample from well C and in some samples from each of the other wells, and its presence is suspected in yet other samples where positive recognition is not possible. It is distinguished from detrital feldspar primarily by the presence of idiomorphic forms against cavities in the rock together with its water-clear appearance. Both orthoclase and microcline have developed as crystallographically continuous outgrowths on detrital grains of potash feldspar and also in open cavities as idiomorphic crystals not continuous with any detrital grain visible in the thin section. Albite occurs as idiomorphic crystals in voids (pl. 1, *A*), but no albite outgrowths on detrital feldspar have been recognized. All three varieties of secondary feldspar have been observed in the same thin section.

Determinations of the feldspars were made in thin section with the universal stage. The indicatrix and poles of visible crystal faces, cleavage planes, and twinning planes were plotted on equal-area projections and determinations made as described elsewhere (Gilbert and Turner, 1948). The faces most commonly developed are the basal and side pinacoids, {001} and {010}; the unit prisms, {110} and {1$\bar{1}$0}, the pyramid, {$\bar{1}$11}, and dome, {$\bar{1}$01}, are common; whereas the prisms, {130} and {1$\bar{3}$0}, and dome, {$\bar{2}$01}, have been observed on only a few crystals. Twinning according to the albite law is visible in some of the larger crystals of secondary albite and microcline but is uncertain or lacking in small crystals. Where detrital microcline is rimmed by secondary microcline, the twinning commonly continues across the boundary into the secondary rim.

There can be no doubt that water-clear idiomorphic feldspar outgrowths attached to cloudy detrital grains and equally clear euhedral crystals in open cavities are both secondary; but there are other water-clear feldspars, apparently uniform throughout and having tight interlocking contacts with surrounding detrital grains of all kinds, which may also be secondary. By careful examination and tilting the stage to appropriate angles, one or two small crystal faces can be observed on a few of these latter crystals where minute voids occur along their contacts; others have only

their water-clear appearance to suggest their secondary origin. The writer is not prepared to classify such anhedral feldspars as definitely secondary, but it seems likely that they are. If feldspar has crystallized in pores of the sandstones, as is certain, some such pores may well have been filled completely by water-clear anhedral feldspar molded against the surrounding detrital grains.

Dolomite.—Dolomite is present in most of the samples from well B and in some from well F. Commonly it occurs as scattered rhomb-shaped crystals in the clay matrix or in voids, but here and there granular aggregates of the rhomboidal grains completely fill the pore space between detrital grains. Although its occurrence is not confined to the clay matrix, dolomite rhombs are much more numerous in the clay than in open pores. Apparently the clay matrix afforded a more favorable environment for the crystallization of dolomite than existed elsewhere in the rock; likewise dolomite tends to form in altered biotite more commonly than in open pores (pls. 3, *E*, and 4, *C* and *D*). However, there is no constant association of these minerals, and many samples containing both detrital clay and abundant biotite do not contain dolomite.

The writer would hesitate to say that dolomite never occurs in these sandstones as anhedral grains; but wherever positive identification has been made, this mineral occurs in idiomorphic or partly idiomorphic crystals bounded by the unit rhombohedron $\{10\bar{1}1\}$. Identification of the mineral as distinct from calcite was made in grain separates on the basis of specific gravity and refractive index and in thin section by measurement with the universal stage of the angle between the optic axis and the direction of a ray (e') having the index of refraction of adjacent quartz or balsam (Gilbert and Turner, 1948). After experience had shown that the idiomorphic carbonate was invariably dolomite, the idiomorphic habit was used as a basis for identification.

Calcite.—With the exception of samples from well A, calcite occurs in most of the sandstones studied, but its amount varies greatly. In some samples it is the only cement and completely fills the pore spaces between the detrital grains (pl. 1, *C*), and in such cases it is either medium granular or composed of very large crystals each uniformly oriented over an area sufficient to enclose many detrital grains. Elsewhere, only a few calcite grains, invariably anhedral and usually filling two or three adjacent pores, are present in a slide (pl. 2, *A*, and fig. 2). There is no constant association of calcite with dolomite; the calcite occurs both in those sandstones devoid of clay and in those containing abundant clay and, unlike dolomite, has not formed in the clay matrix but is restricted to what were apparently open pores in the original rock. No idiomorphic forms have been observed on calcite, but lamellae parallel to the flat rhombohedron $\{01\bar{1}2\}$ were commonly seen.

Some detrital grains of quartz and feldspar have been penetrated by calcite —a relation that can usually be correlated with crystallization of the carbonate along fractures or cleavage in the detrital grains. In some such cases the calcite has wedged apart the sand grains (pl. 1, *B*). Replacement of quartz or feldspar by carbonate, either dolomite or calcite, was not observed and is certainly not typical in the sandstones studied.

Kaolinite.—Partial recrystallization of the detrital clay is common, and the product is either a granular aggregate or several large crystals, commonly showing

a radial structure where the cleavage is inclined at a high angle to the plane of the thin section. Tentatively, this recrystallized clay has been identified as kaolinite. It is biaxial and negative with a medium optic axial angle, and the acute bisectrix (X) is essentially normal to the single cleavage. The birefringence is low, and the refractive index of the fast ray (a) is a little greater than the high refractive index of quartz. Its constant association with the detrital clay matrix suggests that this is a reasonable determination.

That the kaolinite is indeed a secondary mineral seems certain. The largest grains of it, particularly those showing radial structure, are so oriented and molded around detrital grains of quartz and feldspar as to preclude any suggestion that they, too, are detrital. Nor do they show any of the parallel orientation or distortion so typical of the detrital mica in these rocks.

Anatase.—Although it is not abundant enough to constitute an important cement, anatase is a secondary mineral characteristic of this suite of sandstones. In some samples it forms as much as 1 per cent by weight of the rock. It is readily recognized as idiomorphic crystals typically tabular parallel to the basal plane {001} but occasionally pyramidal and having a yellowish color. Single euhedral crystals line some of the voids in the rocks (pl. 1, *D* and *E;* fig. 1), and cloudy aggregates between detrital grains constitute a local cement. The observations made have not certainly proved any particular mode of origin for the anatase; but because a little sphene is present in heavy residues from some of the samples, it may be assumed that anatase has formed from the recrystallization of the titania present in sphene. Also a few crystals present in altered biotite suggest that some of the anatase may have formed from the recrystalliza-

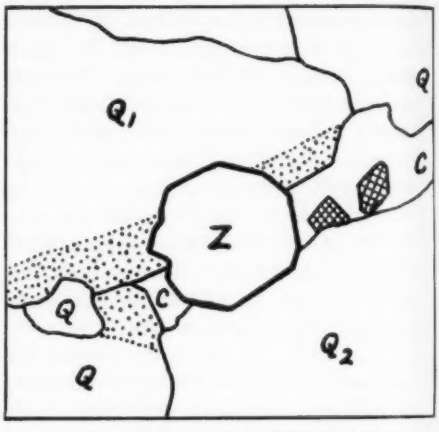


FIG. 1.—Tracing of subidiomorphic zircon (Z) partly embedded in detrital quartz (Q_1 and Q_2) and partly surrounded by secondary quartz outgrowths (*stippled*). Cross-hatched grains are anatase crystals in cavity (C).

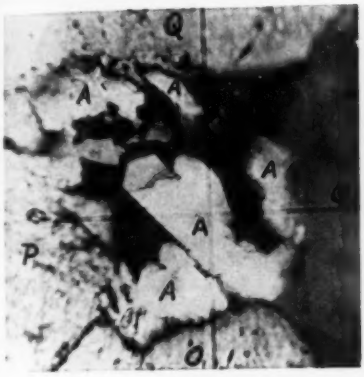
PLATE 1

A, Photomicrograph of idiomorphic albite (A) developed in pore space between detrital grains of quartz (Q), orthoclase (O), and plagioclase (P). Photograph taken under crossed nicols with the universal stage tilted about 25°, with the result that only the central albite crystal is in focus and shows its habit. McAdams sand (S3-10C); magnification 275×.

B, Photomicrograph of detrital plagioclase (Ab_{90}) surrounded by detrital clay matrix and wedged apart by secondary carbonate crystallized along the basal cleavage. Puente sandstone (S3-3F); magnification 250×.

C, Photomicrograph of loosely packed sand grains (mostly quartz and feldspar) cemented by a continuous calcite matrix. Gatchell sand (S3-10B); magnification 50×.

D and *E*, Photomicrographs (*D*, crossed nicols; *E*, plane polarized light) of subidiomorphic zircon partly embedded in detrital quartz and partly surrounded by secondary quartz outgrowths. McAdams sand (S3-5C); magnification 175×. See also fig. 1.

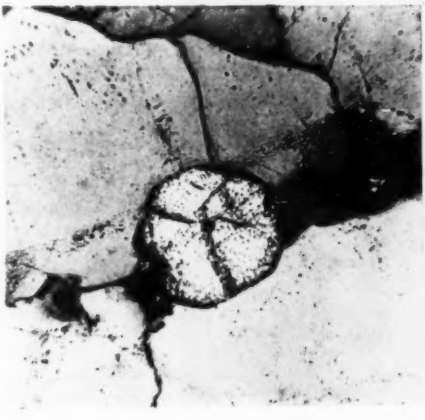


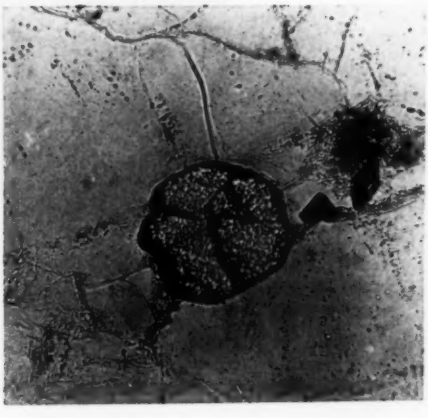
A

B

C

D





E

Cementation of reservoir sands

A

B

C

D

Cementation of reservoir sands

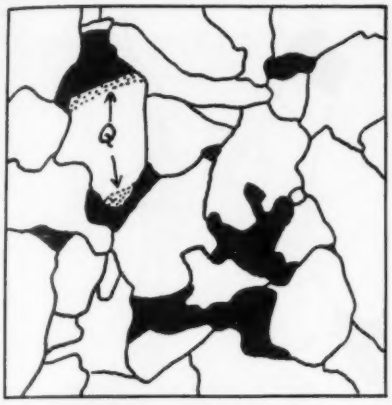


FIG. 2.—Tracing illustrating local calcite and also the interlocking relations of detrital quartz and feldspar in the McAdams sand (S_3=10C). Calcite (*black*) is uniformly oriented throughout and is molded over small quartz outgrowths (*Q*, *stippled*).

tion of titanium oxide in biotite. No other titanium-bearing minerals have been noted.

Barite.—Barite was found only in the shallowest sample from well A where it is a local cement, occurring as a single optically continuous grain that fills the original pores throughout a considerable portion of a thin section (pl. 2, *D*).

Pyrite.—The mineral identified as pyrite is opaque, fine grained, and has the usual color of pyrite, but it could conceivably be marcasite. It is not abundant in any sample but occurs in very small amounts in all of them. Typically it forms tiny microcrystalline aggregates (microconcretions) less than 100 microns in maximum diameter, but its occurrence as a local cement in one thin section was noted.

Glauconite.—A few grains of this mineral occur in the clay matrix in samples S_3-5A, 6A, 2B, and 3B. It has the usual cloudy green appearance typical of the mineral in thin section.

MUTUAL RELATIONS BETWEEN SECONDARY MINERALS

General statement.—Where, as is commonly the case, several secondary minerals can be observed in a single thin section, their mutual relations, except in the cases of barite and pyrite, have been carefully examined. In many sections one mineral is constantly idiomorphic with respect to another—a relation capable of at least three alternative interpretations. It could conceivably arise by simultaneous crystallization (as in metamorphism) under conditions such that one mineral has a greater tendency to assume its own crystal outline than the other; or it could reflect a time sequence of crystallization, in which the idiomorphic mineral crystallized first; or possibly the idiomorphic mineral is the later and has replaced other minerals (Krynine, 1948, fig. 12). Available evidence is still inconclusive except for cal-

PLATE 2

A, Photomicrograph illustrating local calcite cement and also the interlocking relations of detrital quartz and feldspar in the McAdams sand (S_3-10C). Calcite is uniformly oriented throughout and is molded over small quartz outgrowths (*Q*). Magnification 80×. See also fig. 2.

B and *C*, Photomicrographs (taken with plane polarized light and crossed nicols) illustrating (1) secondary quartz outgrowth molded around idiomorphic orthoclase (*F*) and (2) calcite (*arrow*) crystallized on top of idiomorphic quartz outgrowths. The clear orthoclase (*F*) is bounded by the crystal forms {110}, {001}, and {101} and is surrounded by an outgrowth of detrital quartz (Q_1). The crystal faces bounding the triangle of calcite in the center of the photograph are rhombohedron faces on quartz outgrowths from detrital grains Q_1 and Q_2 and are not rational faces of the calcite. McAdams sand (S_3-7C); magnification 90×.

D, Photomicrograph of barite cementing detrital quartz grains in the Gatchell sand (S_3-1A). The mineral having high relief is barite and is in optical continuity throughout the area of the photograph. Magnification 40×.

cite, some of which is undoubtedly later than the other secondary minerals. Calcite not only is consistently anhedral but occupies the central portions of cavities whose margins are lined by other secondary minerals.

The observed relations suggest the following general conclusions for the sandstones studied:

1. Calcite is definitely later than secondary quartz and feldspars; but in a few samples (pl. 1, *C*, for example), where calcite is the only significant cement, it may have crystallized early and inhibited the development of any other secondary minerals.

2. Some secondary feldspar crystallized simultaneously with secondary quartz although some probably crystallized before the quartz.

3. Dolomite crystallized before secondary quartz and calcite.

4. Anatase crystallized before most of the calcite and probably before the quartz outgrowths.

5. Kaolinite, formed by recrystallization of detrital clay, probably formed after deep burial during the same general period when many of the other secondary minerals crystallized, but its relations to them are obscure.

6. Pyrite and barite are thought to have crystallized early among the secondary minerals.

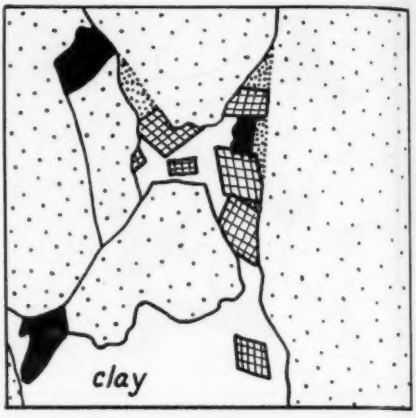


FIG. 3.—Tracing slightly idealized from plate 3, *A*, to indicate the relations determined by tilting to various angles on a universal stage but not clearly evident at any one angle of tilt as in the photographs. Dolomite rhombs (*cross-hatched*) are molded against detrital quartz (*wide stippling*); quartz outgrowths (*close stippling*) are molded against rhombohedron faces of several dolomite crystals. Blank areas in the sketch are detrital clay; black areas are cavities.

The secondary minerals listed above include some not observed by Waldschmidt (1941, p. 1858) in sandstones of the Rocky Mountain region; but quartz, dolomite, and calcite were listed by him as having formed in the order given. The author's results, therefore, differ from Waldschmidt's in that the relative order of crystallization of quartz and dolomite is reversed and also in that some of the calcite in the California sandstones may

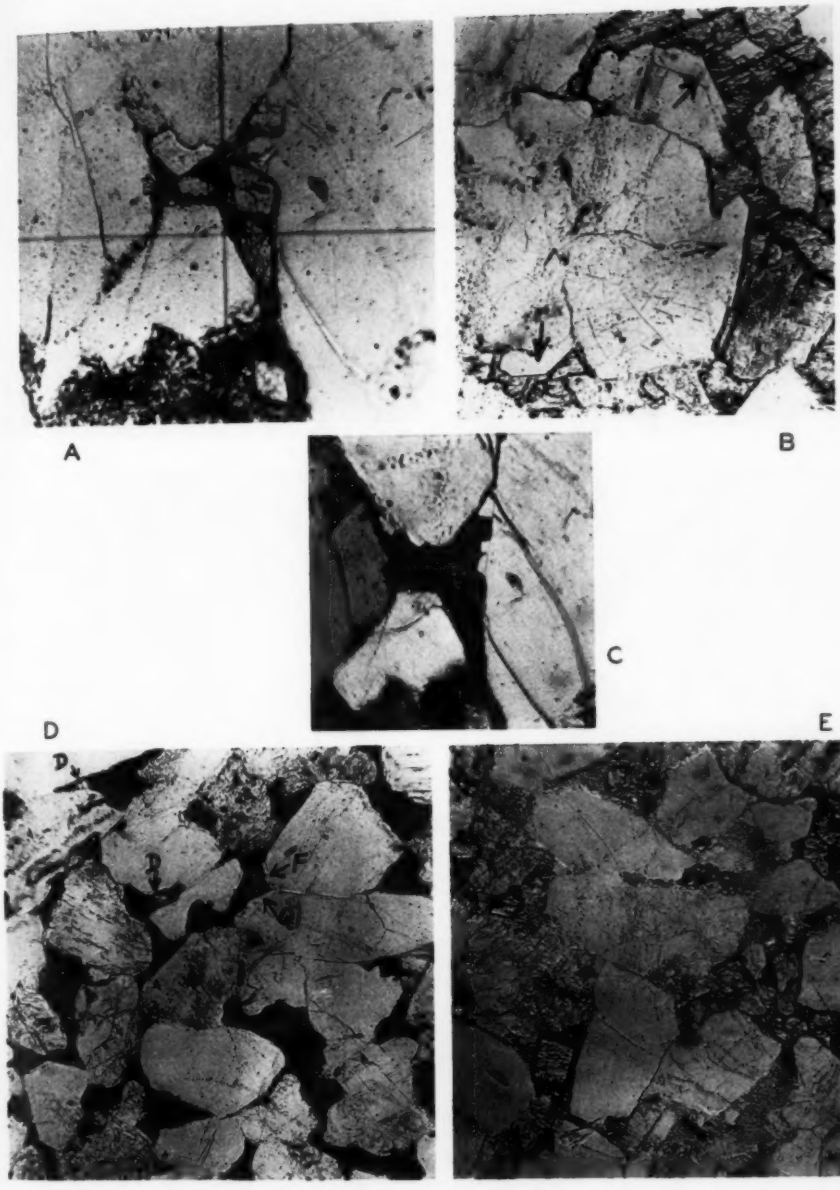
PLATE 3

A and *C*, Photomicrographs illustrating the relationship between dolomite and secondary quartz outgrowths in Puente sandstone (S3-1F). Secondary quartz outgrowths are clearly evident in photograph *C* taken under crossed nicols. Magnification of *A*, 110×. See also fig. 3.

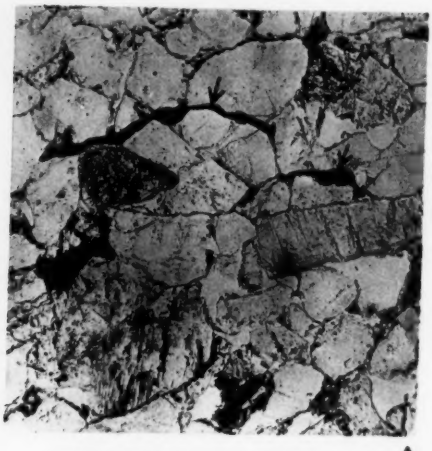
B, Photomicrograph of calcite (*high relief*) surrounding detrital quartz grains with secondary outgrowths (*arrows*) in McAdams sand (S3-1C). The outgrowth in the upper left actually has three crystal faces visible, but only one is apparent at the angle of tilt used for the photograph. Magnification 52×.

D, Photomicrograph of well-sorted Gatchell sand (S3-9B) with open pores shown in black. Detrital grains of quartz and feldspar tightly packed but not typically interlocking (compare pl. 4, *A* and *E*) and very slightly cemented. Incipient outgrowths of quartz (*Q*) and orthoclase (*F*) are shown by arrows; two small dolomite crystals (*D*) in open pores are also indicated. This is the most permeable sample studied and is as porous as any. Magnification 40×.

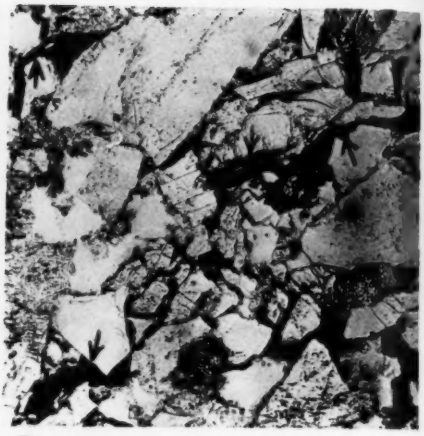
E, Scattered rhombs and granular aggregates of dolomite in detrital clay matrix of Gatchell sand (S3-2B). Magnification 40×.



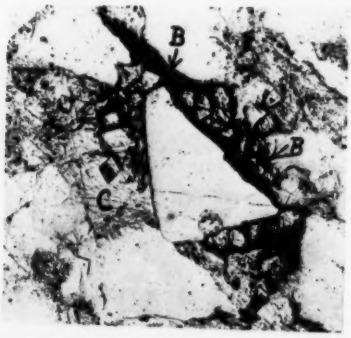
Cementation of reservoir sands



A



B



C

D

E

F

Cementation of reservoir sands

be somewhat earlier than secondary quartz.

Quartz and feldspars.—Secondary quartz and feldspars occur together in all samples from well C (McAdams sand) and in some samples from other wells. In every case the relation between them is the same, the feldspar being idiomorphic in contact with the quartz. This relation applies alike to orthoclase, microcline, and albite against quartz. As previously indicated, however, the writer considers that the periods of crystallization of these two minerals—quartz and feldspar—have overlapped somewhat although the feldspar perhaps tends to be the earlier.

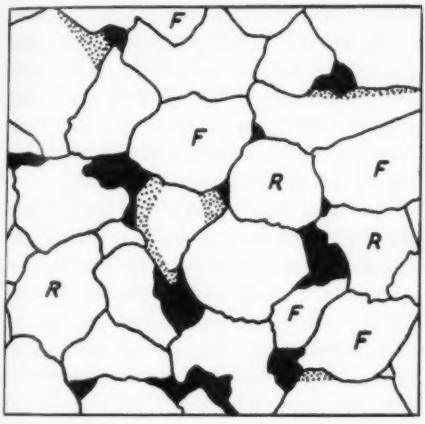


FIG. 4.—Tracing showing idiomorphic quartz outgrowths and tightly interlocking texture of detrital grains in McAdams sand (S3-3C). Unlabeled grains are detrital quartz, stippled areas are quartz outgrowths, black areas are cavities; *F* represents detrital feldspar, and *R* indicates fine-grained rock fragments.

The relation between secondary quartz and albite crystallized in the same cavity is illustrated by a thin section of the deepest sample from well C (S3-10C). Plate 1, *A*, is a photograph of the albite in this cavity taken on a universal stage with a tilt so high that only the albite is in focus. Several pure albite crystals having Baveno habit project into the cavity, and none is in crystallographic continuity with any detrital grain visible in the thin section. The crystals appear to have crystallized on top of thin outgrowths of secondary quartz, as if a little quartz had crystallized ahead of the albite, but the quartz outgrowths have also partly surrounded the albite crystals and are molded against well-formed faces of the feldspar (Gilbert and Turner, example 4). This relation is interpreted as the result of essentially simultaneous crystallization of quartz and albite.

A relationship between secondary quartz and orthoclase is illustrated in plate 2, *B* and *C*, where a distinct out-

PLATE 4

A, Photomicrograph illustrating the interlocking texture of detrital quartz and feldspar grains and showing one greatly distorted crystal of detrital biotite (*arrows*) in McAdams sand (S3-8C). Magnification 42×.

B, Photomicrograph of detrital biotite (*arrows*) distorted by the tight packing of Puente sandstone (S3-9F). The texture is not typically interlocking, and considerable detrital clay is present. Magnification 42×.

C, Dolomite rhombs replacing biotite (*B*) and also embedded in calcite cement (*C*). Gatchell sand (S3-4B); magnification 58×.

D, Dolomite rhombs embedded in continuous calcite cement. Gatchell sand (S3-10B); magnification 42×.

E, Photomicrograph showing idiomorphic quartz outgrowths and tightly interlocking texture of detrital grains in McAdams sand (S3-3C). Crystal faces on the outgrowths from the central quartz grain include the prism and both rhombohedron forms. Magnification 54×. See also fig. 4.

F, Photomicrograph (taken under crossed nicols) of distorted plagioclase in Puente sandstone (S3-5F) having a detrital clay matrix. Strain and radial and concentric fractures in plagioclase (P_1) appear to center around penetrating point of quartz grain (*Q*); twin lamellae bent and radial cracks developed in plagioclase (P_2). Magnification 75×.

growth of quartz is molded against three well-developed faces—the forms {001}, {$1\bar{1}0$}, and {$\bar{1}01$}—on a crystal of orthoclase projecting into a void. Where the quartz outgrowth is in contact with calcite and projects into the unfilled portion of the cavity, typical prism and rhombohedron faces of quartz are clearly seen.

Quartz and calcite.—These two minerals, both secondary, are commonly in contact. Typically the calcite is anhedral and molded against the idiomorphic forms of quartz outgrowths (pls. 2*A*, *B*, *C*; 3, *B*; and fig. 2), and the only reasonable interpretation of this relation is that the quartz crystallized first. The detrital grains were enlarged and the open pores of the sandstone thus partly filled by secondary quartz; later calcite crystallized in some of the remaining voids and filled them completely. Such a relationship has been observed many times in these sandstones. However, it is not always demonstrable by means of ordinary microscopic technique, for proof requires that the crystal faces forming the boundaries between quartz and calcite be tilted into sharp focus and identified as belonging certainly to one or the other of the two minerals. This can readily be done with a universal stage. A pertinent example is illustrated in plate 2, *B* and *C*, where what appears to be a rhombohedron of calcite is surrounded by quartz outgrowths from two detrital quartz grains. This "rhombohedron" proves, however, to be bounded by rational faces (the form {$10\bar{1}1$}) of the quartz outgrowths having no relation whatsoever to normal faces of calcite (Gilbert and Turner, 1948, example 2).

In certain other rocks in which calcite is very abundant and fills the space between detrital grains, the calcite may have crystallized earlier. In such rocks secondary quartz outgrowths have not been found although they are present in closely adjacent samples of the same formation where calcite is less abundant. This suggests that locally where calcite is very abundant it crystallized early, completely cemented the rock, and inhibited the growth of other secondary minerals. Further evidence is found in samples like that illustrated in plate 1, *C*, where detrital grains in a continuous calcite cement do not touch one another, in contrast to the close packing of detrital grains in similar samples not so completely cemented (pl. 3, *D*). This may indicate that the abundant calcite cement crystallized early before tight packing of the detrital grains occurred.

A single case (sample S3-4B) where secondary quartz may have replaced calcite has been observed. The calcite surrounds an idiomorphic quartz crystal greatly elongated parallel to one of the rhombohedrons, instead of the usual prism, and is strictly parallel to one of the cleavages of calcite. Admittedly, as an alternative to the suggested replacement of calcite by quartz, this relationship may be interpreted as calcite molded against a quartz crystal of abnormal habit with the rhombohedrons of the two minerals in parallel orientation.

Quartz and dolomite.—Although dolomite and quartz outgrowths commonly occur in the same sample, they have rarely been observed in contact. Plate 3, *A* and *C*, and figure 3 illustrate the mutual relationships of dolomite and secondary quartz. Dolomite rhombohedrons in a void containing some clay are molded against detrital quartz grains around the cavity, whereas a secondary outgrowth of quartz on one side of the cavity is molded against the rhombohedron faces of dolomite as though it had crystallized after the carbonate. This re-

lationship, like that between quartz and feldspar, is subject to alternative interpretations; either the dolomite crystallized ahead of the secondary quartz or the two minerals crystallized simultaneously. The writer favors the first of these interpretations, especially in view of the observed relationships between dolomite and calcite which suggest that dolomite may have formed even before the early calcite. A third alternative, namely, that the dolomite replaced the secondary quartz, is untenable; if this had happened, the dolomite should show euhedral boundaries against the detrital quartz as well as against the quartz outgrowths. Indeed, dolomite in contact with detrital quartz and feldspar is invariably molded against the surfaces of those grains; although what appear at first to be penetrations of detrital quartz by idiomorphic dolomite have been observed in many samples, tilting of the stage has shown in every case that the actual relationship is one in which the dolomite is simply attached to the surfaces of the detrital grains.

Dolomite and calcite.—Wherever these two minerals are in contact, idiomorphic dolomite rhombohedrons are embedded in anhedral calcite cement. This relationship is illustrated in plate 4, *C* and *D*. One of these examples (pl. 4, *D*) is from a sample (S3-10B) in which calcite is very abundant and probably had crystallized early. Clearly, the dolomite rhombohedrons in calcite may be explained either as a replacement of calcite by dolomite or, alternatively, as dolomite crystals formed early and later surrounded by calcite cement. The evidence is inconclusive. The dolomite rhombs have no observed consistent orientation with respect to the enclosing calcite, as might be anticipated in the event of the suggested replacement. Furthermore, whether associated with calcite or occurring in clay-filled cavities or in association with biotite in rocks free of calcite, dolomite occurs in part as idiomorphic rhombs attached to detrital quartz and feldspar and also as apparently perfect isolated crystals. The mutual relationships of dolomite and calcite with respect to secondary quartz indicate that dolomite formed ahead of the calcite in most samples.

Dolomite and kaolinite.—The secondary clay mineral, thought to be kaolinite, here and there contains rhombs of dolomite. In one case the cleavage of the kaolinite appeared bent around the dolomite crystals as though the carbonate had crystallized later and made space for itself by physical distortion of the kaolinite; in other cases no such relationship was observed, and there is no indication as to which mineral is the earlier. Dolomite, which tends to occur most commonly in the clay matrix, may have replaced the kaolinite itself or it may have replaced the detrital clay matrix before recrystallization produced the kaolinite.

Anatase.—Most of the anatase seen in thin sections is in aggregates of minute crystals clustered together in cavities; less commonly it occurs, as in plate 1, *D* and *E*, figure 1, in larger individual crystals along the margins of the cavities. Generally its relationship to other secondary minerals is not evident; but in several cases anatase crystals attached to detrital quartz grains are surrounded by and probably are earlier than calcite. Because a few minute crystals have been surrounded by quartz outgrowths, the anatase was probably formed early among the secondary minerals.

PREFERRED ORIENTATION

In order to determine whether there is any preferred orientation of quartz in the

most tightly packed and cemented sandstones, the positions of the optic axes in three hundred quartz grains in each of several thin sections were determined with a universal stage. Plotted on an equal-area projection net, a random orientation is indicated by all these measurements. Figure 5 is a typical result.

Measurements of the orientation of optic axes in dolomite rhombohedra likewise indicate a random orientation in those few slides that contain abundant dolomite. Detrital mica, however, tends to be oriented parallel to the bedding, as would be expected.

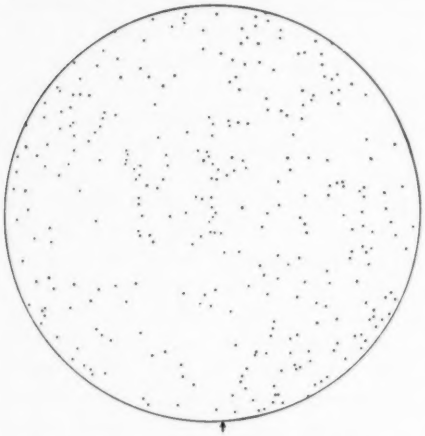


FIG. 5.—Equal-area projection of optic axes in 300 quartz grains (sample S3-3C).

TEXTURE OF THE SANDSTONES

CLASSIFICATION

Typically the sandstones examined are tightly packed; that is, the sand grains are arranged with respect to one another so that minimum bulk volume and porosity is approached. That this tight packing is the result of grain adjustments made under the pressure of deep burial is suggested by the distorted form of detrital biotite grains bent around and squeezed between the more rigid sand grains of quartz and feldspar (pl. 4, *A* and *B*). In some of the sandstones the detrital grains have intimately interlocking and often minutely serrated contacts, which cannot be referred to simple mechanical packing under pressure, but which strongly suggest some partial solution along grain contacts (pl. 4, *A* and *E;* fig. 4). Distortion by fracturing of such interlocked grains, as is illustrated in plate 4, *F*, is not common or typical, but undulatory extinction is observed in many grains. Waldschmidt (1941, pp. 1859–1863) has described and illustrated similarly interlocking quartz grains in the sandstones of the Rocky Mountain region; but in the California sandstones, feldspars and rare minerals like zircon (pl. 1, *D* and *E;* fig. 1), as well as quartz, are involved in the interlocked fabric.

Classified according to texture, the sandstones fall into two broad categories, namely, those in which the sand grains are more or less tightly packed but not typically interlocked and those in which interlocked contacts between detrital grains dominate the fabric. When each of these types is further subdivided according to the character of cementing material, a relation between textural types and character of cement is apparent. Interlocked textures are found in rocks cemented largely by secondary quartz, together with some feldspar, whereas those sandstones without typically interlocked contacts between detrital constituents are uncemented or are cemented by clay either alone or with carbonates. Waldschmidt also noted that interlocked texture was typically associated with relatively large amounts of secondary quartz.

The textural classification given in table 1, based on degree of packing and interlocking of detrital grains and on the

nature of cementing material, is satisfactory for the California sandstones and is intended to apply only to those rocks. But it can probably be extended and modified to give a more general classification as the need arises. There are, as might be expected, gradations between the various textural types indicated. Sandstones of class II (not typically interlocked) commonly contain some grains that are mutually interlocking and may also contain small amounts of secondary quartz and feldspar; and those of class III (typically interlocked) may contain grains that are not interlocking. Nevertheless, a division into these classes can be made by brief inspection of thin sections if only the dominant textural mode is sought.

In sandstones, classified as loosely packed, where the detrital grains appear to be separated by a continuous calcite cement (pl. 1, *C*), the apparent separation between sand grains is not large; indeed, when viewed in thin sections cut at random, an apparent separation between many grains is to be expected even though they are in actual contact at some points. The designation "loosely packed" seems appropriate simply by comparison with the more closely packed sand grains in other rocks belonging to textural class II. Very widely separated sand grains more or less evenly distributed through a calcite matrix (sandy limestone), a textural type described and illustrated by Waldschmidt (1941, pl. X and pp. 1863–1866) from the Jurassic and Cretaceous sandstones of the Rocky Mountains, have not been observed in the California sandstones; such rocks probably would not fit into the textural classification given in this paper.

Three well-sorted sandstones (S_3-7B, 8B, and 9B), representing several feet of well B, consist of very tightly packed sand grains with very little cement of any kind (pl. 3, *D*). These samples are the basis for the textural class II, A. They are the most porous and permeable samples studied, but the fact that the highest porosity in any of them is but 27 per cent indicates that they are indeed tightly packed. The contrast in texture between these three samples and the loosely packed, calcite cemented sandstone (S_3-10B, pl. 1, *C*) 8 feet deeper in the same well is noteworthy because the samples all lie so close together in the same formation and indicates that marked textural differences may be found in a single formation.

TABLE 1

TEXTURAL CLASSIFICATION OF SANDSTONES STUDIED

I. Sand grains rather loosely packed
   A. Calcite cement (pl. 1, *C*)
II. Sand grains tightly packed but not typically interlocked
   A. Poorly cemented (pl. 3, *D*)
   B. Cemented by
      1. Clay (pl. 4, *B*)
      2. Clay and subordinate carbonates
      3. Calcite and subordinate clay
III. Sand grains typically interlocked (pl. 4, *A* and *E;* fig. 4)
   A. Cemented by*
      1. Quartz
      2. Quartz and some calcite
      3. Quartz with a little clay

* Secondary feldspar has been observed in small amounts in sandstones of this textural type and is typically present in textures III, A, 1 and 2.

Other tightly packed sandstones included in textural class II are better cemented, the pore spaces between sand grains being largely filled with clay or with clay and dolomite; a few contain calcite cement and most of them include a small amount of secondary quartz. In contrast, not only are samples from well C and some from well A tightly packed but the sand grains are interlocked. All these samples, classified in textural group III, contain relatively large amounts of

secondary quartz and some feldspars, and many of them contain some calcite or clay as well. But the consolidation of these interlocked sandstones has been accomplished not alone by the cementing substances but also by the mutually molded contacts of the *detrital* grains.

ORIGIN OF THE INTERLOCKED FABRIC

The interlocked fabric as a whole is thought to result from differential solution between detrital grains, combined with the complementary outgrowth of secondary minerals in the voids. This is the origin suggested by Waldschmidt (1941, pp. 1859–1863) for a similar texture observed in the quartz sandstones studied by him, and it seems just as applicable in the present case. Differential solution at points of contact between quartz grains in the St. Peter sandstone has also been suggested by Lamar (1928, pp. 47–48) to account for certain pits observed on the surfaces of detrital quartz grains. The typical association of secondary quartz and feldspars with the interlocked fabric strongly supports the idea that these minerals are indigenous to the rock, being formed by partial solution of detrital grains under pressure at points of contact and precipitation of the dissolved substances at places of lower pressure in the voids. Tight, minutely serrated contacts between detrital grains and apparent penetration of one by another without physical distortion are features that can be explained only by postulating some sort of solution along grain contacts, as described recently by Sloss and Feray (1948, pp. 3–14). Certainly, an indigenous source for secondary quartz and feldspars appears more likely than the alternative that quartz and feldspars were precipitated by ground waters which brought the necessary substances in solution from some outside source, a source not connected with igneous activity. The ground waters required would have to be complex solutions of very slightly soluble substances. Their existence, therefore, is very unlikely and, moreover, would not explain why the deposition of the secondary minerals is so closely correlated with solution along the boundaries of the detrital minerals of similar composition.

The existence of clay between the sand grains would tend to prevent or make less effective the mechanism of differential solution and complementary deposition just outlined. Compact clay tends to transmit more uniformly the stress due to overburden and thus to reduce the heterogeneity of the stress and its concentration at points of solid contact between sand grains. Indeed, if sufficient clay is present, the sand grains may not touch each other at all. Thus it is to be expected that interlocked detrital quartz and feldspar together with secondary outgrowths will, in general, be found only here and there in clay-cemented sandstones.

The foregoing outline is only the most general expression of what must be a most complex process involving a great variety of factors about which little is now known. The writer is not prepared to make a detailed analysis of what the process may involve, but enumeration of some of the factors which undoubtedly are involved will serve to emphasize the complexity of the problem. Such are: the general stress condition in the grains as conditioned by the degree of confinement of the pore fluid, the depth of burial, the shapes of individual grains, and the manner in which the grains are packed and touch each other; anisotropy of the minerals composing the individual grains together with the orientation of individual grains with relation to one another and

to the directions of applied stress; partial molal volumes of the minerals involved; surface tension effects; relative compressibility of liquid and solid phases; and composition of the pore fluid. Complex though the process may be, the evidence visible in the sandstones examined amply justifies consideration of such a mechanism to account for cementation in many sandstones. It may well be questioned, however, whether the suggested process is effective under a wide variety of conditions and in a wide variety of fragmental rocks deeply buried or whether it is an effective process only under particular conditions and in certain types of sandstone. Future investigation will have to answer that question. For the process to be significantly effective, however, there must be an unequal distribution of stress over the grain surfaces so that solution will occur at points of greatest stress and deposition at places of lesser stress. This condition can probably occur whether or not the pore solution is confined or free to migrate. In any case, the writer envisages the process as being slow and probably as proceding with diminishing effectiveness as the surfaces of contact between grains become larger and larger. It may be that cementation by this method alone is rarely complete. Probably, too, the process would vary in effectiveness with depth of burial, for it is conceived to operate under the pressure induced by loading and under the temperatures to be expected as a result of the normal thermal gradient.

POROSITY AND PERMEABILITY

A relationship between porosity, permeability, and textural and mineralogic type of sandstone is to be expected. Fine grain size and poor sorting (argillaceous sandstone, for example) are well-known syngenetic causes for low permeability; likewise, the postdepositional processes of compaction, cementation, and solution all produce changes in the original porosity and permeability of the deposit. Among the samples examined during the course of this study (table 2) those which have an interlocking texture and are cemented by secondary quartz, feldspar, and some calcite but without any clay (well C) tend to have lower average porosity and permeability than those samples containing compacted clay matrix with or without other cementing materials. The lowest porosity and permeability is shown by a sample loosely packed but solidly cemented with calcite (S_3-10B). As might be anticipated, the highest porosity and permeability occurs in sandstones containing little cement and represented by three samples (S_3-7B, 8B, 9B) from well B. These results apply only to the sandstones studied. Other sandstones may show greater variations in compaction and cementation.

A general measure of the decrease in porosity and permeability caused by differential solution and complementary deposition, resulting in the interlocked texture, is suggested by this study. The three well-sorted, tightly packed sandstones containing little cement of any kind (S_3-7B, 8B, 9B) are comparable in grain size, sorting, and composition with tightly interlocking samples from well C, and they are thought to represent approximately the condition sandstones from well C attained after tight physical packing but before cementation. Thus the difference in porosity and permeability between these two groups of samples (textural classes II, A, and III, A) gives the general order of magnitude of reduction in porosity and permeability in sands such as these, produced by partial solution along grain contacts under pressure and complementary infilling of the

TABLE 2

DEPTH, PERMEABILITY, POROSITY, AND TEXTURE OF THE CORE SAMPLES STUDIED

	Sample No.	Well Depth (Feet)	Permeability (Millidarcys)	Porosity (Per Cent)	Texture* (Table 1)	Average Grain Size†
Well A: Gatchell sand, Middle Eocene	S3-1A	9,069	229	15	II, B, 1	MC
	-2A	9,079	250	14.9	II, B, 1	M
	-3A	9,101	89	13.4	III, A, 3	M
	-4A	9,104	45	12.8	III, A, 3	M
	-5A	9,106	6	12.0	II, B, 1	MF
	-6A	9,112	0.44	9.7	II, B, 1 ?	F
	-7A	9,123	57	12.8	II, B, 1	MC
	-8A	9,133	212	15.4	II, B, 1 ?	MC
	-9A	9,139	29	12.9	III, A, 3 ?	M
	-10A	9,142	88	14.3	III, A, 3	M
Well B: Gatchell sand, Middle Eocene	S3-1B	8,172	99	16.9	II, B, 2	F
	-2B	8,176	84	17.6	II, B, 2	M
	-3B	8,182	240	24.5	II, B, 2	F
	-4B	8,186	20	19.3	II, B, 2	F
	-5B	8,201	254	18.4	II, B, 2	MF
	-6B	8,213	358	19.9	II, A, & II, B, 2	MF
	-7B	8,220	2,020	23.6	II, A	MF
	-8B	8,221	2,180	27.2	II, A	M
	-9B	8,222	2,840	26.9	II, A	MF
	-10B	8,230	0.24	6.7	I, A	F
Well C: McAdams sand, Middle Eocene	S3-1C	12,195	17.8	14.3	III, A, 2	M
	-2C	12,200	3.7	12.2	III, A, 2	MF
	-3C	12,202	9.5	13.1	III, A, 2	M
	-4C	12,207	7.4	11.8	III, A, 2	MF
	-5C	12,221	8.3	12.9	III, A, 2	MF
	-6C	12,224	3.0	12.2	III, A, 2	F
	-7C	12,233	1.7	10.2	III, A, 2	F
	-8C	12,235	2.2	11.3	III, A, 2	F
	-9C	12,237	1.3	10.9	III, A, 1	F
	-10C	12,240	1.7	10.9	III, A, 2	F
Well F: Puente formation, Upper Miocene	S3-1F	10,358	36	16	II, B, 2	M
	-2F	10,471	13	10	Slide torn	.....
	-3F	10,492	17	11	II, B, 2	F
	-4F	10,558	9	9	II, B, 3	M
	-5F	10,617	604	20	II, B, 3 ?	MF
	-6F	10,647	20	14	II, B, 2	M
	-7F	10,649	9	13	II, B, 2	M
	-8F	10,652	25	13	II, B, 2	F
	-9F	10,656	45	12	II, B, 2	M
	-10F	10,805	24	16	II, B, 2	MF

* Texture refers to the textural classification in table 1, p. 13.

† Average grain size refers to the approximate modal diameter of sand grains as estimated from thin-section examination. F = fine sand, 125–250 microns; M = medium sand, 250–500 microns; C = coarse sand, 500–1,000 microns; double letters (MF and MC) refer to sands on the border line between medium and fine or medium and coarse, respectively.

pores by secondary minerals; that is, a change in porosity from more than 25 per cent to between 10 and 15 per cent and a change in permeability from more than 2,000 millidarcys to approximately 10 millidarcys. During cementation by the process suggested, porosity would decrease progressively and slowly, not only because the pore space is progressively filled, but also because the solution at points of contact between grains permits closer packing. The process might proceed farther than is indicated by the present samples, perhaps reaching essential completion, or it might be halted at some intermediate point; but wherever it occurs, a very significant decrease in porosity and permeability is to be expected. In clay-cemented sandstones a decrease in porosity and permeability will certainly result from compaction. The magnitude of this reduction cannot be estimated from the present study.

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THE FACIES CLASSIFICATION OF ROCKS: A CLUE TO THE ORIGIN OF QUARTZO-FELDSPATHIC MASSIFS AND VEINS[1]

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ABSTRACT

The formation of quartzo-feldspathic rocks—principally pegmatites—is discussed from the viewpoint of thermodynamic stability of minerals and mineral associations.

Most quartzo-feldspathic rock bodies, migmatites, and pegmatitic veins encountered in folded chains exhibit mineral associations which indicate a formation at temperatures below which silicate melts cannot exist.

Data from a granulite facies area in western Greenland show that, even at the relatively high *P-T* conditions that prevailed there, the granitic component in the system was unable to form melts. Furthermore, pegmatites and quartzo-feldspathic massifs[2] usually possess mineral associations in harmony with the degree of metamorphism prevailing in the surrounding region. In high-grade areas the pegmatites—independent of their bulk chemical composition—show high-temperature mineral assemblages; in low-grade areas low-temperature assemblages occur in the pegmatites.

Because the melting curve of a magma is definitely determined by the bulk composition of the system (at constant pressure), the logical conclusion must be that most pegmatites, veined gneisses, migmatites, and several acid massifs were formed by some metamorphic-metasomatic processes in which silicate melts were unable to co-operate.

THE PROBLEMS

The origin of deep-seated quartzo-feldspathic rocks encountered in regional metamorphic areas is still an unsolved problem.

Very often the same quartzo-feldspathic rock or pegmatitic vein is interpreted as a magmatic crystallization product by one author, as a metamorphic-metasomatic product by another, while a third considers it to be the product of an anatectic pore melt or granitic ichor.

If there were a large overlap of the *P-T-X* (*X* = composition) fields of rock-making silicate melts and of solid minerals, the different viewpoints might be explained by supposing that the several authors defend somewhat one-sided views on a complex phenomenon in part magmatic and in part metamorphic. (The term "metamorphism" here comprises all endogenic processes taking place at submagmatic *P-T-X* conditions.) However, we have good experimental as well as field reasons for believing that magmatism is confined to temperatures above 600°–900° C. (depending on the content of water and other "volatiles" in the silicate system). Only above these temperatures should silicate minerals and melt coexist.

Below these temperatures the melt may be substituted for by saturated but dilute aqueous fluids. These saturated solutions should contain less than 1 or 2 per cent of silicates because common rock-forming minerals are not very soluble in water (Ingerson and Morey, 1937). On the other hand, silicate melts cannot absorb more than 10 per cent of water (Goranson, 1931, 1936, 1937); consequently, the system: rock-making silicate melts—water does not form a continuously miscible series.

The liquid or gaseous solutions occurring in pores and fissures in crystalline silicate rocks certainly may be charged with such easily soluble constituents as NaCl, KCl, alkali silicates, various solu-

[1] Manuscript received March 19, 1948.

[2] The term "massifs" as used in this paper means large, homogeneous bodies of deep-seated rocks.

ble fluorides, sulphates, etc. (Newhouse, 1932). However, as such compounds practically never occur in the crystalline state in the common silicate rocks, we can conclude that the rock solutions are very seldom saturated in these constituents. Furthermore, it has never been proved experimentally or theoretically that aqueous solutions of such easily soluble constituents are completely miscible with the rock-making silicate melts. Therefore, in harmony with experimental data, we can draw a simple diagram (fig. 1) showing the *P-T* fields of magmatism and metamorphism, respectively.

In the magmatic field, melts and gases are involved in the formation of rocks. In the metamorphic field, the rock-forming processes take place in the solid state with or without a coexisting dilute fluid which is very different from a silicate magma both in composition and in physical properties.

It is reasonable to expect, therefore, that the rock or mineral assemblages formed from magma—either by magmatic differentiation or by partial anatexis and subsequent crystallization—would be quite different from those formed by metamorphism. Only if progressive metamorphism brings a rock to the boundary between metamorphism and magmatism will the products of these two processes be identical.

There are seldom different opinions as to whether basic rocks are metamorphic or magmatic. Regarding the metamorphic basic rocks, however, it is in many cases difficult to decide whether they were emplaced in a magmatic or in a submagmatic state. A given massive or foliated low-grade amphibolite or greenstone, which everybody agrees is metamorphic, may be interpreted as an orthoamphibolite, as a para-amphibolite, or as a metasomatic amphibolite by different authors; but nobody will consider this low-grade rock as crystallized directly from a magma.

The case of quartzo-feldspathic rocks is quite different. Some investigators believe that these rocks have crystallized directly out of a magma; others believe that metamorphic recrystallization alone has taken place. The reason for disagreement is clear. The quartzo-feldspathic minerals are stable within a wide range of pressures and temperatures, from those

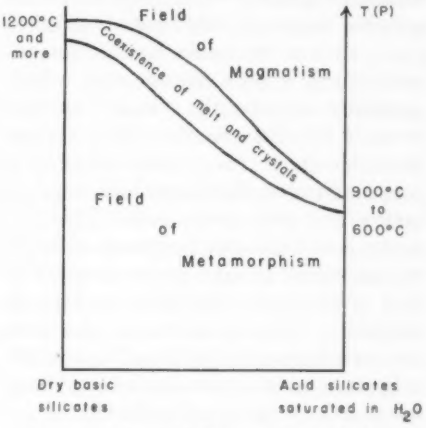


FIG. 1.—Schematic diagram of the relation between magmatism and metamorphism.

of magmatic rocks down to the low greenschist facies. The common minerals in a granite or an acid quartz-diorite, therefore, are not indicative of the *P-T* conditions at which these rocks are formed. However, in several cases it is also possible to determine the mineral facies or pressure-temperature conditions which quartzo-feldspathic rocks represent (Eskola, 1921, 1939). These determinations suggest that most granites, granodiorites, and pegmatites encountered in gneissic areas formed at pressures and temperatures so low that very few of these rocks can be interpreted as primary magmatic products.

Some of the objections to the view that most quartzo-feldspathic bodies and veins are the product of a "progressive" magmatic differentiation from a juvenile basic magma support the "regressive" magmatic differentiation hypothesis. The partial anatexis and palagenesis of J. J. Sederholm, P. Eskola, Tom. F. W. Barth, and others explain the formation of some granitic or granodioritic bodies, some pegmatitic veins, and the phenomenon of granitization by assuming that during progressive metamorphism, a regressive magmatic differentiation takes place, that is, the easily melting components form a pore silicate melt which gradually absorbs the "basic" components in the rock complex. At a certain favorable stage this re-fused material is supposed to generate larger homogeneous bodies and pegmatitic veins. This hypothesis of regressive magmatic differentiation seems to take proper account of two of the main objections to juvenile magmatic differentiation: (1) the ratio between deep-seated acid and basic rocks is opposite to that between acid and basic lavas and (2) the space problem.

However, there are several objections to both these magmatic hypotheses. The problems fall into two main groups, namely, (1) the kinetic-structural problems and (2) the thermodynamic stability problems.

The kinetic-structural problems involve the movement or transfer of the rock-forming substances: Has it been a mechanical bodily motion or a diffusion? The thermodynamic stability problems involve the state of the system from, or in, which the problematic quartzo-feldspathic rocks form.

THE KINETIC-STRUCTURAL PROBLEMS

Let us consider only briefly the kinetic-structural problems. Coarse-grained and isotropic fabric of rocks is commonly considered as evidence of magmatic origin. Nevertheless isotropic coarse-grained massive rocks can form during metamorphic recrystallization or metasomatism, if the rocks are affected by confining homogeneous pressure and given a sufficiently long time of reaction. The epidote-bearing quartz-dioritic or granitic helsinkites and unakites, for example, have been interpreted as primary magmatic rocks (Mäkinen, 1916; Laitakari, 1918; von Eckermann, 1925; and Wilkman, 1928), but the mineral assemblages of these rocks positively indicate a *P-T* field well below that of hydrous silicate melts.

Likewise, numerous "magmatic" cross-cutting and conformable veins of isotropic fabric (some pegmatites, quartz veins, etc.) contain a mineral assemblage indicative of submagmatic conditions. It appears that both the coarse structure and the cross-cutting character of such veins have in many instances been the principal evidences on which investigators have based their conclusion of magmatic origin. For example, Frank L. Hess wrote in 1925 (p. 290), referring to the origin of pegmatites: "In attempts to explain their origin, all investigators seem to be agreed on one point, namely, that the pegmatites are of igneous origin." This was a reasonable statement before Goranson had made his experiments with solubility of water in granitic melts and before we knew much about other possible forces and processes which could form pegmatitic bodies, but Hess's viewpoint is no longer tenable. Even before the limited effect of water on the depression of the melting "point" of magmas was known, investigators (for example, Hess, 1925; Landes, 1933) observed evidences of metasomatic alteration of pegmatites. The commonly ac-

cepted conclusion was that the "simple" pegmatitic bodies underwent metasomatic alteration after their crystallization from a magma. This alteration was then assumed to be due to magmatic rest solutions of unknown composition and physicochemical character.

Commonly, larger bodies of quartzo-feldspathic rocks encountered in gneissic and regional metamorphic areas show foliation which is often explained as flow in a magmatic melt containing some early-formed crystals (Cloos, 1936). It is difficult to determine whether a foliated structure is due to flow in partly crystallized magma or in a solid rock. However, in a partly crystallized moving magma the parallelization of the minerals should be caused by form orientation of elongated or flaky minerals. On the other hand, deformation of the crystal units (e.g., quartz and feldspar) so commonly observed in deep-seated rocks implies a crystalline state of the rock body itself at the time of deformation.

If the foliated structure proves deformation in the solid state, the rock may, of course, be a recrystallized orthogneiss. The texture of deep-seated rocks, therefore, cannot be used as positive proof of the state of the substances during the emplacement of the rock material. Common features of folded mountain chains are quartzo-feldspathic massifs exhibiting structures conformable with their gneissic or schistose surroundings. Such conformable contacts show that the differences in fluidity among the several rocks have been small, as might be expected, if the folded and deformed complex were a complex of crystalline rocks rather than rocks intermingled with quartzo-feldspathic melts. If the general conformity is explained by assuming that the high pressure makes the viscosity of the melts approach the viscosity of the crystalline rocks, new difficulties for the magmatic hypothesis will arise. The magmatic hypothesis must assume that granitic melts—eventually charged with up to 10 per cent of water and other volatiles—are able to penetrate crystalline rocks during regional metamorphic conditions and form confined pegmatitic bodies in nongranitic rocks, e.g., amphibolites (Andersen, 1931). This permeability seems to be so great that it cannot possibly be due to any circulating pore ichor possessing a viscosity comparable to that of the crystalline country rock.

It seems impossible to me for any liquid (even water) to penetrate mechanically most metamorphosed rocks because they are compact and contain only an intergranular or mosaic pore system of molecular dimensions. Supermolecular fissures and ruptures which in places open up during mechanical deformation of rocks would be discontinuous and therefore unable to conduct circulating fluids. Furthermore, supermolecular openings in rocks are thermodynamically unstable and will be closed rapidly by plastic flow and diffusion in the strained zone around such fissures.

The larger fissures which extend throughout metamorphic terranes are, of course, able to convey magmas as well as watery solutions provided that the fissures are in communication with the proper sources. However, pegmatites are commonly not in communication with fissures of this type.

Lenticular conformable pegmatites so commonly encountered in gneissic schists (for example, the Black Hills pegmatites [Fisher, 1942, 1945]) appear to have pushed the country rock in front of their expanding boundaries, thus proving that the mechanical pressure in the pegmatite bodies has been greater than in the sur-

rounding gneisses. Consequently, the introduced material has, during the formation of the pegmatite, moved from low toward high mechanical pressure. This would be physically impossible if the transferred material were a melt or hydrous liquid. Diffusion of individual atoms, molecules, or ions, however, can easily explain the formation of these pegmatites because molecular particles will automatically diffuse toward high mechanical pressure when the chemical potential, or the vapor tension, is lower at the site of high pressure than in the surroundings (Ramberg, 1944*b*, 1944*d*).

If silicate melts are able to penetrate crystalline rocks in a fashion required by the theory of magmatic origin of pegmatites, veined gneisses, etc., why is basic magma never found penetrating metamorphic rocks in the same diffuse manner? It is well known that basic magmas are more fluid than acid melts, and undoubtedly water and other volatiles decrease the viscosity of a basic magma just as they decrease the viscosity of acid silicate melts. It seems obvious that some kind of transfer of substances other than the simple bodily flow of magmas and solutions is required.

THE PROBLEMS OF THERMODYNAMIC STABILITY

Pegmatites as key rocks.—The mineral assemblages of some quartzo-feldspathic massifs belong to the same facies as that shown by the country rock. This may be explained by postmagmatic metamorphic recrystallization, although it is not clear why such rocks, if of magmatic origin, should be subjected in all cases to regional metamorphism.

However, pegmatites (commonly considered as crystallized rest liquors from granites) usually occur as "primary" vein bodies only rarely found deformed. It is therefore important to note that these "primary" pegmatitic rocks often contain a mineral suite that not only indicates submagmatic conditions but also denotes the same *P-T* values as those found in the wall rock. Thus, even if pegmatites are magmatic, considerable mobility in subsolidus silicate systems is required to explain the ability of coarse-grained, commonly cross-cutting pegmatites to recrystallize in a completely new metamorphic form.

It is generally assumed that pegmatites are due to watery rest solutions expelled from crystallizing magmas. In this connection, let us consider a comparatively low-grade metamorphic area where the "mother" granite is a recrystallized unakite with epidote, acid plagioclase, microcline, quartz, micas, etc., and the cross-cutting, undeformed pegmatites are of granodioritic composition. The metamorphic assemblage in the granite indicates a temperature perhaps some hundred degrees below the solidification "point" of any hydrous granitic magma (fig. 2). The hypothetical watery pegmatitic solution which crystallized as cross-cutting veins during the last stages of metamorphism must, if it was expelled from the granitic magma, have been wandering throughout the region from the time of crystallization of the magmatic granites to the consolidation of the pegmatites. Moreover, the unakites represent rather low degrees of metamorphism; and, therefore, the hypothetical pegmatitic solutions must have persisted during a long period of regressive metamorphism. Thus they must have interacted continuously with the metamorphosed minerals, and I see no way to decide now whether these solutions were of magmatic or metamorphic-metasomatic origin.

The importance of pegmatites in the problems under discussion makes a brief

description of these rocks desirable. It is well known that there exists every transition among the several types of pegmatitic veins or segregations in regional metamorphic areas. In composition they range from basic oligoclase pegmatites through granodioritic, syenitic, and true granitic pegmatites to pure quartz bodies. Other more rare types are, on the one hand, the Li pegmatites and, on the other, the phlogopite-apatite-pyroxene-hornblende pegmatites.

Although the prevailing view is that many of the rare minerals and elements so commonly found in pegmatites are characteristic of the latest crystallization product of a magma, this view cannot be considered proved adequately. As the magmatic origin of pegmatites was not questioned (Hess, 1925), it was assumed that the occurrence of rare minerals and elements in them proved that the magmatic rest solutions carried these elements. Most rocks, sedimentary as well as igneous and metamorphic, contain several of the rare elements in spectroscopically detectable amounts (B, U, V, Be, etc., in sediments; Sc, etc., in amphibolites, etc.), so we usually have no difficulty in ascribing sources for most rare elements encountered in pegmatites. An enrichment of such rare elements in certain pegmatites by means of metamorphic-metasomatic processes (selective diffusion) is a priori no more impossible than progressive or regressive magmatic differentiation.

However, the idea of some leaching from the country rocks has been accepted only if the mineralogical composition of a pegmatite (garnet, cordierite, andalusite, kyanite, etc.) deviates too much from that reasonably expected of magmatic rest liquors (Andersen, 1931; Bjørlykke, 1934; etc.).

The form and the structure of pegmatites change within wide limits. Pegmatites in places penetrate gneisses in the form of plane-parallel dikes, but these are of limited extent as compared with true magmatic dikes such as rhomb porphyry, diabase, etc. Many pegmatites occur as confined lenticular bodies of either conformable or cross-cutting character. Completely irregular masses are also common. Pegmatites are most commonly sharply defined bodies, although gradational boundaries exist between the pegmatite and the country rocks.

The size ranges from microbodies to masses several hundred meters across. However, pegmatites larger than 5–10 m. wide and some hundred meters long are comparatively rare.

The texture within a pegmatitic body may be heterogeneous. A feldspar border phase and a quartz core are typical but are absent from many pegmatites.

The mineral assemblages denote a very wide *P-T* range from about 600° C. to perhaps 100° C., or from the granulite- or pyroxene-hornfels facies down to greenschist facies.

Although exhibiting such a diversity of properties, pegmatites have many characters in common, some of them not easy to define. The one character which most pegmatites have is occurrence as rather small bodies—usually of quartzo-feldspathic composition—with textures and composition distinguishing them from the country rock.

Another significant characteristic which justifies grouping of this type of rocks is their occurrence in regionally metamorphosed areas, apparently having some important relation to regional metamorphism. This fact was emphasized by O. Andersen (1931), although he considered the pegmatites to be chiefly of magmatic origin.

Our present knowledge of mobility of

substances by diffusion under regional metamorphic conditions gives a more plausible explanation of the striking connection in space and time between metamorphism and formation of pegmatites.

METAMORPHISM IN FOLDED MOUNTAINS

The association of granites, gneisses, and pegmatites in regional metamorphic areas indicates that the problem of the origin of all these types of rocks can be solved only by field and petrological studies in more or less eroded folded mountains. Folded mountain chains vary widely in character, but there are some important properties that all folded mountains have in common. On an average, for example, the degree of regional metamorphism increases from the low-grade superficial borders toward the high-grade central and deeper parts.

In the deep roots of eroded folded mountains the degree of metamorphism appears to be uniform over large areas. Thus, in the deeply eroded parts of the pre-Cambrian and Caledonian chains, rocks belonging to the epidote-amphibolite facies, the amphibolite facies, and the granulite facies cover thousands of square miles. A granulite facies area in western Greenland, for example, mapped by Danish expeditions in 1946, 1947, and 1948, extends about 150 km. across the strike between Holsteinsborg and Egedesminde. Investigations of the mineral associations show that the *P-T* conditions were astonishingly uniform throughout this vast area, although rocks vary widely in composition.

The vast anorthosite-birkremite field in western Norway described by C. F. Kolderup (1914, 1933) and Tom. F. W. Barth (1945) should also be interpreted as a regional metamorphic complex formed, or at least recrystallized, under *P-T* conditions corresponding to the granulite facies. Kolderup (1933) considered these rocks as "no doubt magmatic," although his description indicates that the whole field has been subjected to regional metamorphism, as there is no difference in mineral facies between the basic noritic rocks and the acid hypersthene granitic gneisses, massifs, and pegmatites.

A. W. Groves (1935) explains the hypersthene gneisses of Uganda, Africa, as a high-grade metamorphic facies of the surrounding "common" gneisses belonging to amphibolite facies. T. H. Holland (1900) interpreted the classic charnockite-norite complex of India as a vast magmatic series. His evidences were cross-cutting dikes and structural properties which now cannot be accepted as proof of magmatic origin. The norite dike (Holland, 1900, pp. 228–230) which cuts a gneiss lying in contact with the charnockite series is probably a diabase dike which was recrystallized, together with the host gneisses, in the granulite facies. There are several examples of the same phenomenon in western Greenland.

Holland's detailed rock descriptions show that—as in Uganda, Norway, Ellesmerland (Bugge, 1910), and western Greenland (tables 1, 2, 3)—the members of the norite-charnockite "kindred" correspond to the same *P-T* conditions. I am thus convinced that the classic Indian area contains a series of high metamorphic rocks belonging to the granulite facies.

The areal extent of the amphibolite facies and the epidote-amphibolite facies in eroded folded chains depends on the definitions of these facies. Pentti Eskola, who introduced the concept of mineral facies (1921, 1939), distinguished between the epidote-amphibolite facies and the amphibolite facies on a less accurate conception of the stability relationship

between epidote and plagioclase (Ramberg, 1944*a*, 1944*b*). Epidote is stable at relatively higher temperatures than was supposed when the epidote-amphibolite facies was defined. More important, however, is the fact that intermediate and acid plagioclase are stable far below the uppermost limit of the stability field of epidote (fig. 2). Thus, if the epidote-amphibolite facies is to include the whole stability field of epidote, the epidote-amphibolite facies would have a very large areal extent in gneissic regions. The amphibolite facies, on the other hand, will be narrowly restricted because the *P-T* gap between the stability fields of rhombic pyroxene and epidote is rather small (figs. 2–3). It may be better, therefore, to set the boundary between the epidote-amphibolite facies and the amphibolite facies at the lower *P-T* boundary line of diopsidic pyroxene. This line corresponds approximately to an equilibrium between epidote and plagioclase of composition An_{30} under regional metamorphic conditions (fig. 2). Thus defined, the highest part of epidote-amphibolite facies (epidote in equilibrium with An_{20-30}) and the amphibolite facies cover very large areas in eroded folded mountains of pre-Cambrian, Caledonian, and Hercynian age.

In less eroded folded chains the change of degree of metamorphism is more rapid and irregular to the extent that we are above or outside the main field of quartzo-feldspathic gneisses. The degree of metamorphism in less eroded mountains is considerably more dependent on the large-scale tectonics so that, for example, highly metamorphosed complexes of gneisses are interfolded in, and thrust over, schists of a lower degree of metamorphism.

Pentti Eskola (1939) considered the greenschist facies, epidote-amphibolite facies, and the amphibolite facies as the "normal" facies of regional metamorphism, placing, among others, the granulite facies outside this "normal" sequence. However, investigations of several areas—Groves (1935), Kolderup's and Barth's descriptions of the Egersund area in Norway (1914, 1933, 1945), Adams' description of Ceylon (1930), Hietanen's description from Finland (1947), and my unpublished investigations in Greenland—show that the granulite facies should be placed in the "normal" sequence of regional metamorphism. This facies represents the highest *P-T* conditions that prevailed during regional metamorphism.

The granulite facies has, as we know, its greatest extension in old pre-Cambrian areas, although it is also found in younger chains. In the Caledonian chain in Norway, for example, the granulite facies is found in two situations: (1) in the roots of the chain in the west coast district (the Bergen areas and farther north) and (2) in the form of overthrust rocks: the Bergen-Jotun "kindred" of V. M. Goldschmidt (1916).

Even before the last-mentioned complex could be interpreted as metamorphic-metasomatic rocks formed in the granulite facies, Goldschmidt and others found that they were thrust—in the solid state—over less metamorphosed rocks. Their origin now seems clearer. They were formed, or at least recrystallized, under granulite facies conditions in the Caledonian root, along the west coast of Norway, and have not recrystallized to lower facies during their comparatively rapid tectonic elevation.

With increasing degree of metamorphism in folded mountains, the process of granitization (or perhaps, more correctly, quartzo-feldspathization) is intensified. Quartzo-feldspathic massifs, either in the form of large conformable

batholiths (basement granites, diapire granites) or in the form of rather homogeneous folded layers among the more heterogeneous schists and gneisses, appear as one crosses the eroded mountains toward the central parts.

Very typical features are the pegmatitic bodies which apparently develop in the epidote-amphibolite facies (usually not far below the stability temperature of diopside) and continue throughout the epidote-amphibolite, the amphibolite, and the granulite facies.

Field work in western Greenland indicates that the pegmatites are typical of epidote-amphibolite and amphibolite facies areas, whereas in the granulite facies area the number and size of pegmatites seem somewhat less. For the Greenland area this can be interpreted as a pressure effect. Fissures and other low-pressure places activating pegmatitic crystallization do not easily form during the heavy pressure prevailing in granulite facies areas. However, whether or not this is a general phenomenon cannot be determined because no granulite facies area has yet been adequately described.

In greenschist facies areas and in the actinolite-schist facies the pegmatites seem to be represented by quartz veins and alpine veins which exhibit minerals of low-temperature origin. It is, however, worth while to note that in alpine veins, also, quartz and feldspars are the principal minerals, with some chlorite, calcite, etc. (Koenigsberger, Niggli, Parker, 1940).

The phenomenon of granitization and other types of metasomatism is highly varied and polyphase in detail. Whereas some basic and nongranitic rocks have been gradually imbued with quartzo-feldspathic material reaching, successively, the composition of a granite, a granodiorite, or a quartz-diorite, some marbles and amphibolites remain for a long while unaltered. In other cases rocks have even been basified by removal of quartzo-feldspathic material or by introduction of ferromagnesian elements. D. Reynolds (1946) has very clearly described and emphasized this process of basification. Quantitatively, basification plays a less important role than quartzo-feldspathization. Qualitatively, the process is an important detail of regional metamorphism and metasomatism.

The distances over which substances migrate in one manner or another through crystalline rocks, altering them here and there, and consolidating as confined pegmatitic veins at other places, are not easy to determine. We observe the result of an intricate complex of processes usually without any means of determining the earlier stages. As a rule we cannot definitely decide whether a quartzo-feldspathic gneiss is the result of mere recrystallization or of metasomatic replacement.

One of the first proofs of large-scale introduction of quartzo-feldspathic substances into schists was offered by V. M. Goldschmidt in his paper on the Stavanger area (1920). In addition to a gradation in rock composition at different distances from a granitic body, another proof of the penetration of crystalline rocks by foreign materials is the presence of pegmatites in metamorphic amphibolites and other nongranitic rocks. If structure alone be considered, migmatites and agmatites could be explained by the hypothesis of an invading or anatectic magma having intermingled with the old rocks. However, the usual mineral facies of migmatites, agmatites, and similar rocks belongs to the field of metamorphism and thus proves that the movement of matter has not taken place in the form of silicate melts.

THE MAGMATIC THEORY VERSUS THE METAMORPHIC-METASOMATIC THEORY

The foregoing brief description outlines the principal features of metamorphic areas. The main problem to be discussed is: Are granites and granodiorites mainly magmatic, i.e., intruded from juvenile or anatectic melts during the orogeny; and are the pegmatites the crystallized residual melts or anatectic liquor; and the migmatites, veined gneisses, etc., a solidified mixture of these melts and the remnants of the older rocks? Or are these features typical of most metamorphic areas, due principally to different processes—taking place largely in the submagmatic state?

The latter possibility may be briefly outlined as follows: Sediments and lavas overlying a "granitic" substratum in a geosyncline are folded and deformed together with the substratum itself. The "younger" granites and granodiorites in the folded chain are then partly granitic substratum, which is interfolded and intruded in a crystalline state into the superlayers, and partly crystallized arkoses and acid lavas. The acid rocks are in part formed by metasomatism, which involves diffusion among the different chemically incompatible rocks, and up from the granitic substratum. According to this theory, the pegmatites are formed by metamorphic-metasomatic processes without the participation of silicate melts.

This theory, of course, does not deny the occurrence of granitic or acid melts where the temperature was high enough. But, because the temperature of even the highest grade of metamorphism (granulite facies) is less than that of magmatism, the theory considers magmatism negligible in the formation of acid rocks found in regionally metamorphosed areas.

Several reasons for this view will be discussed later. Field observations strongly impress one with the continuity between rather homogeneous granitic massifs and low-grade schists. Such a continuity would not be the case if the rock-forming agency were in part a concentrated granitic melt and in part a very dilute watery solution. However, if the processes were all submagmatic, a transition from unaltered to completely granitized rocks would be expected.

The common regional increase of temperature is supposed to be due in part to the geothermal gradient and to radioactivity, in part to exothermic chemical reactions between incompatible rocks, and in part to the liberation of heat of consolidation where the activated diffusing atoms, molecules, and ions consolidate.

The requirements of the magmatic hypothesis should be that (1) the granodioritic-granitic substances are introduced in the form of silicate melts; (2) there is in every case evidence that mechanical forces have acted on the melt to move it in the required direction; (3) the melt can penetrate solid crystalline rocks to form veined gneisses, "augen"-gneisses, pegmatites, and granitized rocks; (4) the mineral assemblages of the granitic rocks and veins correspond to the solidus temperature of the magma in question and are the same for all rocks of the same composition (with the same content of "volatiles") and vary with composition according to the rules of magmatic crystallization; and (5) the temperature in the crystallizing massifs and pegmatites as a rule be different from that in the regional-metamorphic surroundings (because the crystallization temperature of a magma is determined by its composition and pressure and must be independent of the physical and chemical conditions in the surroundings).

The requirements of the metamorphic-metasomatic hypothesis are that (1) the quartzo-feldspathic bodies be formed below the field of magmatism, i.e., below approximately 550°–900° C.; (2) the mineral association in the "granitic" bodies (massifs and pegmatites) correspond approximately to the degree of regional metamorphism in the area where such bodies are situated (some smaller or larger deviations are to be expected owing to chemical instabilities, to exothermic and endothermic interactions, and to different velocities of reactions of different rocks and minerals); (3) the temperatures of formation of the rocks (indicated by the mineral assemblages) be independent of the chemical composition; (4) there be some relation between chemical composition of a pegmatite and the enclosing rocks; (5) in every case there exist chemical potential differences which can explain the diffusion of atoms, ions, and molecules through rocks in the required directions (if supermolecular fissures exist, flow of watery solutions or flow of gases will take place); (6) the diffusion coefficients for the several atoms, ions, or molecular compounds in rocks be considerably different, so that selective diffusion can explain metamorphic-metasomatic differentiation (for example, the formation of granite pegmatites in amphibolites); (7) the diffusion through the different pathways in rocks be rapid enough to produce the observed metasomatism; and (8) the crystalline plasticity be sufficient to permit the considerable movement which takes place during formation of most migmatitic gneisses. The fluidity of the quartzo-feldspathic material must be greater than that of the basic rocks.

Points 1, 2, 3, and, in part, 4, are discussed here, but points 5–8 are expounded more thoroughly in other papers.

The solution of the problem lies in the determination of the *P-T* conditions of formation of various rocks and mineral assemblages. The most adequate method seems to be the investigation of stable mineral associations according to the principle of mineral facies, although every type of geological thermometer may be used.

In most deep-seated regional metamorphic and plutonic rocks the minerals are to a great extent in mutual equilibrium within more or less confined parts of the rocks. The mineral facies is governed by the *P-T* conditions extant during the main period of formation. Minerals formed at *P-T* conditions different from those of the main assemblage are usually not difficult to recognize.

These observations on deep-seated rocks are not always easy to interpret. Special difficulties are presented by the granulite facies formed in the deeper and/or central parts of folded mountains, which retain their high mineral assemblages during elevation of the crust and are often overthrust on low-grade rocks. Metamorphism is by no means a continuous and reversible process which is progressive when the rocks (sediments, lavas, etc.) are depressed and folded down in the "crust" and regressive when they are elevated. Instead, during a period of orogeny, conditions permit metamorphic-metasomatic reactions which reach chemical equilibrium in certain parts of the crust. After these conditions disappear, the power of reaction decreases rapidly enough to prevent extended retrograde metamorphism.

Absence of retrograde metamorphism may be explained in three ways. (1) Hot magmas may be injected, keeping the temperature in the surroundings high and rather constant for a long time. After the melt has crystallized, there follows a decrease in temperature too rapid to permit mineral readjustment to the new

conditions. (2) Catalysts may promote the chemical reactions during the course of the metamorphism. These catalysts may subsequently lose their effect or disappear. (3) Heat liberated during the mechanical and chemical readjustments accompanying the formation of folded mountains may be the main factor in regional metamorphism. In the later stages of the mountain-making processes (the cratogenesis) these readjustments cease and no more heat is liberated, so that the power of reaction falls rapidly with the decreasing temperature.

The temperature declines because of (1) cessation of the exothermic chemical and mechanical equilibriopetal processes and (2) rapid elevation through colder zones extinguishing chemical action.

The power of metamorphic interaction, K, can be expressed as follows:

$$K = A \cdot e^{-q/RT}, \qquad (1)$$

where R is the gas constant, T absolute temperature, A a constant depending on the type of interaction, and q is the molal heat of activation. The quantity q is usually very high, of the order of magnitude 20,000–50,000 cal. (Barrer, 1941). Decreasing temperature, consequently, greatly retards the velocity of interaction between solids.

Calcoferromagnesian minerals undergo many transformations within the wide P-T field between greenschist facies and granulite or pyroxene-hornfels facies. At the same time, quartzo-feldspathic rocks remain seemingly unaltered because quartz, potash feldspar, and acid plagioclase are stable minerals within the whole P-T range mentioned. Biotite and muscovite, the other two important minerals in quartzo-feldspathic rocks, are also stable throughout most of the P-T field of regional metamorphism. Biotite is stable at favorable chemical conditions in parts of the greenschist facies as well as in granulite facies. Biotite is also stable in the pyroxene-hornfels facies, and undoubtedly this mineral can crystallize directly out of a magma. However, the chemical stability field of biotite seems to be small in both the greenschist facies and in the granulite facies.[3]

In the epidote-amphibolite facies and in the amphibolite facies the P-T conditions are most favorable for formation of biotite, and the chemical stability field of biotite is extensive.

The narrowing of the chemical stability field of biotite in the granulite facies is due to the partial splitting of some end members of the biotite series into hypersthene and/or garnet with the liberation of potash feldspar, water, etc.

Muscovite is stable from the lowermost temperatures of metamorphism up to the boundary between the amphibolite facies and the granulite facies, where the mineral is changed to sillimanite and potash feldspar.

The third calcoferromagnesian mineral which occurs in some quartzo-feldspathic rocks is hornblende. Under favorable chemical conditions this mineral is stable throughout the whole range from the actinolite-greenschist facies up to the granulite facies, where it gradually splits up into hypersthene, plagioclase, etc., so that only certain types of hornblende can exist up to the field of magmatism.

The chemical stability field of hornblende, however, changes markedly throughout the different mineral facies. The field is narrow in the lowest grades of regional metamorphism and in the granulite facies, but in most of the epidote-amphibolite facies and in the whole of the amphibolite facies hornblende has a very large chemical stability field.

[3] The chemical stability field of a mineral is definable as the field, or polydimensional space, within which the bulk composition of an assemblage can vary without disappearance of the mineral in question.

Between the amphibolite facies and the granulite facies only aluminous hornblendes rich in iron and/or titanium are stable in quartzo-feldspathic rocks (p. 36). In unsaturated rocks even hornblendes poor in TiO_2 and FeO or Fe_2O_3 are stable in the granulite facies.

The most obvious indication of the change from the amphibolite facies to the granulite facies, or vice versa, in quartzo-feldspathic rocks is no doubt the appearance or disappearance of orthorhombic pyroxene.

Although potash feldspar and acid plagioclase are stable from diagenetic conditions up to magmatism, the feldspars undergo distinct changes in passing from the amphibolite facies into the granulite facies. In granulite facies typical perthite and antiperthite are common (see description by Holland, 1900; Goldschmidt, 1916; Groves, 1935; Adams, 1930; Gevers and Dunne, 1942).

The plagioclase feldspar in the granulite facies has a characteristic greenish-brown color.[4]

In conclusion, there are distinct indicators of the *P-T* change from the amphibolite facies to the granulite facies in most quartzo-feldspathic rocks, but rocks of restricted composition (for example, some biotite granites) do not exhibit any distinct change in mineralogy when they are changed from the amphibolite facies into the granulite facies, or vice versa.

THE EPIDOTE-PLAGIOCLASE AND THE BIOTITE-GARNET EQUILIBRIA

In the large area from the greenschist facies to the granulite facies the most distinct *P-T* indices in quartzo-feldspathic rocks seem to be (1) the continuous equilibrium between plagioclase and epidote or zoisite and (2) the continuous equilibrium between Mn, (Fe, Mg)-garnet plus potash feldspar, and biotite (plus muscovite or sillimanite).

These two continuous equilibrium systems register the whole *P-T* range from the greenschist facies throughout the epidote-amphibolite facies, and the amphibolite facies up to the granulite facies (Ramberg, 1944*a*).

To avoid any misunderstanding, I emphasize that at present only the principal features of these equilibrium systems are known. These known features are, however, sufficient for the use to which they are put in this paper. I hope that enough field and laboratory data can be obtained to give accurately the structure of these two systems.

The following two equations show the transition from anorthite to epidote in potash-rich (3) and potash-free (2) rocks, respectively:

$$\underset{\text{anorthite}}{2CaAl_2Si_2O_8} + \tfrac{1}{2}H_2O \rightleftharpoons \underset{\text{kyanite}}{\tfrac{1}{2}Al_2SiO_5} + \underset{\text{epidote}}{Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{quartz}}{\tfrac{1}{2}SiO_2}, \qquad (2)$$

high temperature; low temperature

density:	2.76		3.50	3.25	2.65
volume:	2·101	$\Delta V \sim 29$cc.	½·50	139	½·23

$$\underset{\text{anorthite}}{4CaAl_2Si_2O_8} + \underset{\text{orthoclase}}{KAlSi_3O_8} + 2H_2O \rightleftharpoons \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{epidote}}{2Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{quartz}}{2SiO_2} \qquad (3)$$

[4] Unpublished chemical tests indicate that the color is due to absorption of about 0.5 per cent FeO and Fe_2O_3 in the feldspar lattice. As the typical greenish-brown Fe-bearing feldspar in the granulite facies is always associated with Fe-rich silicate, such as hypersthene and some hornblendes, probably the high *P-T* conditions of the granulite facies enable iron to enter the feldspar lattice provided that the chemical potential or vapor tension of Fe in the rocks is high enough.

The transition temperature of equation (3) is expected to be somewhat higher than that of equation (2) because muscovite has, in association with potash feldspar, somewhat less partial Al-tension or activity than kyanite.

Figure 2*A*, shows approximately the continuous equilibrium between epidote and plagioclase resulting from equations (2) and (3) when albite is taken into consideration. We may postulate that the curves begin at about 400°–500° C. in the Ca side of the diagram and end at room temperature in the Na side, and field experience indicates that the lines curve much as in figure 2.

It is important to note that in potash feldspar- and muscovite-bearing rocks the plagioclase which is in equilibrium with epidote should be somewhat more acid than in muscovite-free rocks at the same *P-T* conditions, the difference becoming negligible at lower temperatures. Figure 2 does not hold for calcite-bearing rocks.

Qualitatively, we can conclude that increasing H_2O tension in the rocks will displace the equilibrium toward epidote. The ability of epidote to take much Fe into its lattice makes increasing Fe/Al ratio in rocks displace the equilibrium somewhat toward the epidote side. Equations (2) and (3) show also that the equilibria depend on the SiO_2 content, so that in quartz-free rocks the epidote may de stable at higher temperatures than in quartzose rocks.

The only experiments which indicate something about the absolute *P-T* conditions of the epidote-plagioclase equilibrium is the hydrothermal synthesis of anorthite at comparatively low pressures (Niggli and Schlaepfer, 1914).

At 470° C. anorthite repeatedly was formed in these experiments at hydrothermal conditions, thus indicating that epidote or zoisite is not stable at, or above, 470° C. at comparatively low pressure.

The effect of pressure upon equations (2) and (3) cannot be computed correctly until the heat of reaction is known. Some rough estimates may be obtained by using reasonable values of the heat of dehydration of silicates.

Epidote is perhaps the silicate mineral which binds its water most strongly because this mineral, unlike most hydrous minerals, does not lose all its water below 1,000° C. (Smethurst, 1935). Hydrous minerals which apparently bind their water content with much less energy than epidote exhibit molal energies of dehydration of the order of magnitude 20,000–35,000 cal. (Eitel, 1941).

Thus, using a value of 24,210 cal. (equal to 1,000 liter-atmospheres) for the heat of transition of equation (2), we obtain from the Clausius-Clapeyron law:

$$\frac{dT}{dP} = \frac{T_u \Delta V}{Q} = \frac{743 \cdot 0.029}{1{,}000} = 0.021°/\text{atm.}$$

At a depth of 20 km., for example, the transition temperature should increase from 470° C. to about 600° C.

However, 470° is probably too high for the uppermost stability temperature of epidote at low pressure, and it is also likely that 24,210 cal. is too low for the heat of reaction of equation (2). Therefore, the temperature values given here might be above the highest stability boundary of epidote. At least, we have at the present no reason to believe that epidote is stable at higher temperature than those evaluated here.

The volume of water is disregarded in equation (2) because there is every reason to believe that water molecules can migrate rather easily through intergranular spaces in metamorphic rocks, so that the rock pressure does not equal the water vapor pressure.

The simplest equation for the reaction of potash feldspar and garnet during regional metamorphism is

$$\underset{\text{potash feldspar}}{KAlSi_3O_8} + \underset{\text{garnet}}{(Mg, Fe)_3Al_2Si_3O_{12}} + H_2O \rightleftarrows \underset{\text{biotite}}{K(Mg, Fe)_3AlSi_3O_{10}(OH)_2} + \underset{\text{sillimanite}}{Al_2SiO_5} + \underset{\text{quartz}}{2SiO_2} \quad (4)$$

In this equilibrium the Mg/Fe ratio in garnet is purposely less than in biotite (see tables 5, 6), so that the Fe end members react according to equation (4) at somewhat lower temperature than do the Mg members.

Below the degree of metamorphism at which sillimanite reacts with potash feldspar with formation of muscovite, the reaction (4) is changed to

$$\underset{\text{potash feldspar}}{2KAlSi_3O_8} + \underset{\text{garnet}}{(Mg, Fe)_3Al_2Si_3O_{12}} + 2H_2O \rightleftarrows \underset{\text{biotite}}{K(Mg, Fe)_3AlSi_3O_{10}(OH)_2} + \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{quartz}}{3SiO_2}$$

Now, taking the spessartite component of garnet into consideration, we arrive at an equilibrium diagram between (Mg, Fe, Mn)-garnet, potash feldspar, and biotite as shown in figure 2, *B*. In this diagram we know that the equilibrium curve will be displaced upward somewhat by an increase of the Mg/Fe ratio and depressed slightly by a decrease of the Mg/Fe ratio. The correct form for the equilibrium curve is not fully known; it is certain only that it begins in the granulite facies and ends down in the lowermost part of the epidote-amphibolite facies, or in the greenschist facies. (Rocks containing the minerals plagioclase, epidote, garnet, biotite, potash feldspar ± [muscovite and/or kyanite] would be excellent for determining the relative position of the curves in figure 2, *A* and *B*.)

FIELD AND PETROLOGIC OBSERVATIONS

The granulite facies is comprised of rocks which have been affected by the highest *P-T* conditions of regional metamorphism and granitization. This facies of rocks is therefore decisive; for, if we prove that the easiest melted rock-making silicate system (i.e., a granitic system of certain composition) has not been liquid in the granulite facies, it is obvious that silicate magmas cannot exist at lower temperatures of regional metamorphism. Consequently, we may then assume that granites, granodiorites, migmatites, veined gneisses, and pegmatitic bodies exhibiting minerals belonging to the amphibolite facies, and to the epidote-amphibolite facies are either thoroughly recrystallized or are formed by some metamorphic metasomatic processes.

It might perhaps be assumed that volatiles depress the melting "point" of quartzo-feldspathic systems down to temperatures characteristic of the amphibolite and the epidote-amphibolite facies even if we can prove that the rocks in question have not been liquid in the granulite facies. The granulite facies has been considered an exceptionally "dry" one, so that it would be natural to assume that the water content has been insufficient to make a granitic material melt (Goldschmidt, 1916). However, there are some phenomena which are inconsistent with this assumption. For example, under the magmatic theory the coarse structure of pegmatites and the apparent mobility of the pegmatitic material is due to a great concentration of water and other volatiles in the pegmatitic magma. However, in the Greenland pegmatites in

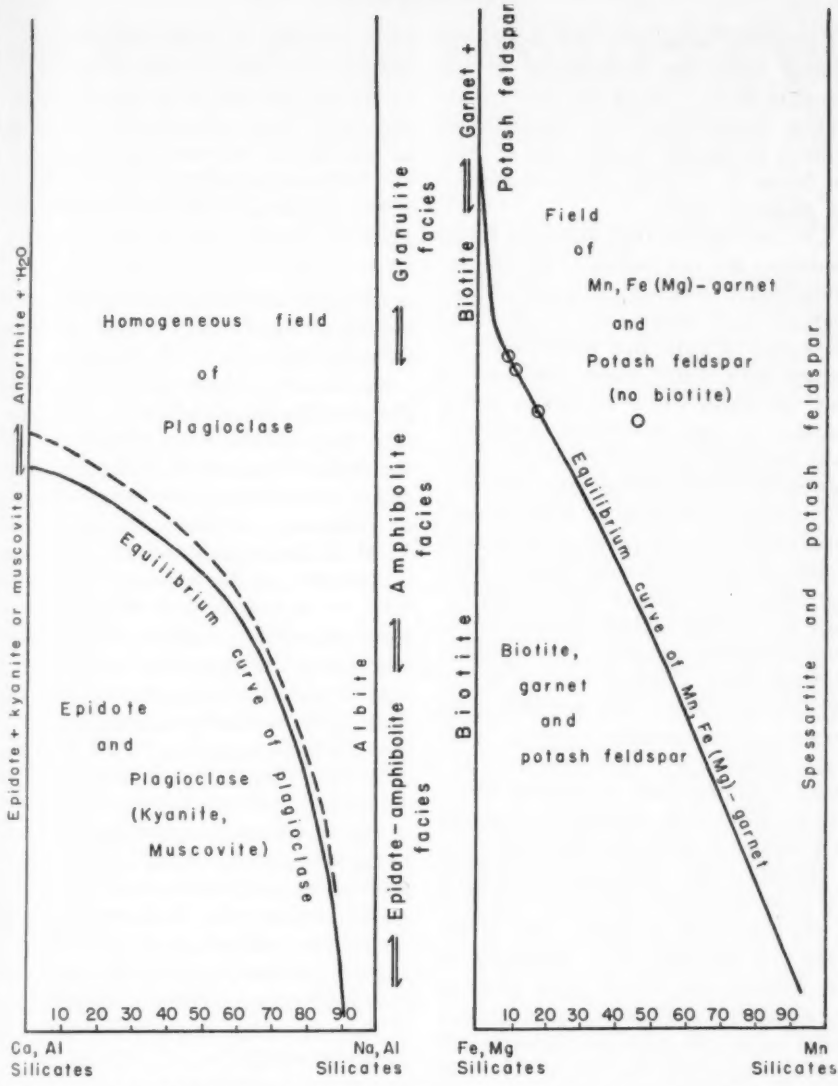


FIG. 2.—*A*, Subsolidus diagram of the plagioclase ⇄ epidote equilibrium. The composition of the system which the diagram represents corresponds to equations (2) and (3), p. 30, with the exception that Ca can be substituted for by Na. The transition temperature between anorthite and epidote corresponds to about 500° C. The solid curve gives approximately the composition of plagioclase in equilibrium with epidote in K-free rocks, whereas the stippled curve represents plagioclase in equilibrium with epidote in rocks containing muscovite and/or potash feldspar.

B, Subsolidus diagram of the biotite ⇄ potash feldspar, garnet equilibrium (eqs. [4] and [5], p. 32). The weight percentage of spessarite in garnets in equilibrium with biotite, potash feldspar (sillimanite, muscovite) is indicated by the equilibrium curve. Garnets from pegmatites in amphibolite facies gneisses in western Greenland are plotted in the diagram (see table 6).

the granulite facies area the pegmatitic mineral suite also corresponds to the granulite facies, proving that the crystallization temperature of a hypothetical hydrous pegmatitic magma was at least not below the temperature prevailing in the granulite facies.

The assumption that granulite facies conditions are not favorable for the introduction of volatiles and water into an anatectic melt seems unreasonable. The absorption of water in a silicate melt increases with water vapor pressure, so that, at places where the water vapor pressure is high, conditions should be most favorable for the formation of silicate melts by increasing temperature.

It seems to me that we must assume that the water vapor pressure in the pore system in rocks is usually higher in the granulite facies than in lower facies despite the smaller content of water in the granulite facies minerals. The expulsion of water from chlorite, biotite, anthophyllite, etc., when they are altered to garnet and hypersthene is due to an increase of the water vapor pressure of hydrous minerals with increasing metamorphism. Thus, in a garnet-hypersthene rock formed in the granulite facies from a chloritic, talc, anthophyllite-bearing low-grade rock, the water vapor pressure in the pores will be higher than in the water-rich low-grade rock. Because both temperature and water vapor pressure are higher in the granulite facies than in lower facies, the granulite facies should actually represent the most favorable conditions for formation of anatectic pore melts.

There is no reason to believe that juvenile magmas are poorer in volatiles where they are intruded into a granulite facies area than where they are intruded in rocks belonging to lower facies. In fact, the opposite is more probable because the high pressure responsible for the granulite facies should prevent more completely the escape of volatiles. Consequently, there seems to be no reason to believe that the melting temperature of a rock-making silicate system is lower in the amphibolite and the epidote-amphibolite facies than in the granulite facies.

Adequate data are not available concerning absolute pressures and temperatures that give rise to the facies.

Wollastonite which has been found in the granulite facies (Adams, 1930; Hietanen, 1947) and also in the highest parts of the amphibolite facies (Eskola, 1915; von Eckermann, 1922) cannot be considered an adequate geological thermometer. V. M. Goldschmidt's well-known calculations give only the highest temperature limit for wollastonite at different pressures (Ramberg, 1946*b*). Wollastonite can form at temperatures below 500° C. regardless of the rock pressure because CO_2 is able to migrate through the pores in metamorphic rocks so that the CO_2 pressure is never fixed in metamorphic rocks. The fact that wollastonite as well as calcite and quartz occur together both in the granulite facies and in the highest parts of the amphibolite facies is in complete harmony with the theoretical considerations outlined above. (R. Kühne, 1932, records wollastonites in association with epidote in Auerbacher marbles.)

The only data on the temperature of formation of the granulite facies are H. von Eckermann's determination for the highest part of the amphibolite facies in Mansjö in Sweden (1922). The association of α- and β-quartz shows the temperature of formation to be about 600° C. This value may serve as the lower boundary of the granulite facies. According to this rather uncertain estimate, hydrous

granitic melts might or might not be stable in the granulite facies of rocks.

However, we shall turn to field, microscopical, and chemical studies of the Greenland rocks and minerals in deciding whether or not granites and pegmatites have been melted in the granulite facies.

GRANULITE FACIES AREAS

A. W. Groves (1935) seems to have been the first to prove that a series of rocks of charnockitic affinity, in Uganda, Africa, are the granulite facies metamorphic derivatives of gneisses belonging to amphibolite and epidote-amphibolite facies. My work on the pre-Cambrian of western Greenland shows that the hypersthene gneisses (enderbitic gneisses) and the noritic rocks there must be interpreted in the same way as the hypersthene gneisses in Uganda.

Rocks belonging to the granulite facies strike W.SW. and cover an area of about 15,000 sq. km. west of the ice cap between Holsteinsborg and the Arfersiorfik fiord south of Egedesminde. North and south of this area are rocks of the amphibolite facies and gneisses belonging to the epidote-amphibolite facies. The rocks of the granulite facies are mostly rather homogeneous enderbitic gneisses containing a certain bluish quartz, brownish-green andesinic antiperthite, orthorhombic pyroxene, ilmenite, and magnetite as the principal constituents. Perthitic potash feldspar, diopsidic pyroxene, garnet, a peculiar Fe- and Ti-rich hornblende, and biotite are also commonly found in the enderbitic gneiss. Only rarely is the potash feldspar content sufficient to make the gneisses mangeritic (Kolderup, 1933) and charnockitic. In this gneissic complex are found bands, lenses, and more equidimensional bodies of basic rocks usually of hornblende noritic composition. Folded layers of marbles, khondalites, kinzigites, and graphite gneisses occur conformably alternating with the acid hypersthene gneiss. Large and small conformable and cross-cutting pegmatites of heterogeneous mineralogical and chemical compositions are commonly scattered in the several gneisses throughout the whole area.

The structure of the complex and apparently also the chemical composition of the rocks are the same as are commonly observed in gneissic areas belonging to the amphibolite and the epidote-amphibolite facies.

Of importance are several noritic bands and lenses in the acid hypersthene gneisses which are interpreted as the granulite facies derivatives of the amphibolitic and epidote-amphibolitic layers, boudins, and deformed dikes found in the gneisses both south and north of the granulite facies area. Farther south along the coast the amphibolitic layers are in turn found to be cross-cutting diabase dikes.

The noritic components in the hypersthene gneiss are, therefore, derived from common diabases. The hypersthene-bearing enderbitic gneiss that commonly includes and penetrates the noritic layers is an activated granulite facies variety of the old hornblende-biotite gneiss which once was invaded by the diabase dikes.

These field observations show that the rocks of charnockitic affinity (norites, enderbites, charnockites) were not formed by magmatic differentiation but by high-grade regional metamorphism. In addition to these briefly stated field evidences, we shall consider the mineralogical evidences in detail.

In the norite-enderbite-charnockite series of Greenland as well as in rocks of other areas (Washington, 1916; Bugge, 1910; Groves, 1935; Parras, 1941; Gevers

and Dunne, 1942) the basic members are rich in hornblende whereas orthorhombic pyroxene is the most common ferromagnesian mineral in the acid members. (Diopsidic pyroxene, biotite, and garnet are commonly found in basic as well as in acid members.)

As emphasized by Groves (1935, pp. 194–200), this is not in accord with the theory of magmatic differentiation, according to which hornblende should crystallize later and at lower temperatures than should hypersthene. According to the facies diagrams of Eskola (1939), we should also suspect our basic hornblende noritic rocks of having consolidated at a lower temperature than the surrounding hypersthene gneisses. The explanation is that all types of rocks are recrystallized, and in part formed, at very nearly the same *P-T* conditions. It is the stability relationships of hornblende which make this mineral form in basic rocks at the same temperature at which hypersthene forms in acid rocks.

The Al-free actinolitic and tremolitic hornblendes are unstable in the highest parts of the amphibolite facies and in the granulite facies; they split up into hypersthene and diopsidic pyroxene:

$$\underset{\text{actinolite}}{\text{low temperature}}\ \ \underset{}{Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2} \rightleftharpoons \underset{\text{diopside}}{\text{high temperature}}\ \ \underset{}{2Ca(Mg, Fe)Si_2O_6} + \underset{\text{hypersthene}}{3(Mg, Fe)SiO_3} + \underset{\text{quartz}}{SiO_2}\,. \qquad (6)$$

The types of hornblende stable in the granulite facies are therefore rather rich in Al (the analyses available show from 8.65 per cent to 13.5 per cent Al_2O_3, according to Groves [1935] and my own unpublished data from Greenland).

We are dealing, therefore, with aluminous "common" hornblendes. The transition from the amphibolite facies to the granulite facies is, among other things, characterized by the following:

$$\underset{\text{hornblende}}{\text{low temperature}}\ \ \underset{}{NaCa_2(Mg, Fe)_4Al_3Si_6O_{22}(OH)_2} + \underset{\text{garnet}}{(Mg, Fe)_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{5SiO_2} \rightleftharpoons \underset{\text{hypersthene}}{\text{high temperature}}\ \ \underset{}{7(Mg, Fe)SiO_3} + \underset{\text{plagioclase}}{NaCa_2Al_5Si_7O_{24}}\,.$$

The rhombic pyroxene-plagioclase side represents the granulite facies. Note that hornblende will be stable at higher *P-T* conditions in SiO_2-deficient rocks than in those which are quartz-bearing. In other words, the reaction

$$\underset{\text{hornblende}}{\text{low temperature}}\ \ \underset{}{NaCa_2(Mg, Fe)_4Al_3Si_6O_{22}(OH)_2} + \underset{\text{garnet}}{(Mg, Fe)_3Al_2Si_3O_{12}} + \underset{\text{hypersthene}}{3(Mg, Fe)SiO_3} \rightleftharpoons \underset{\text{olivine}}{\text{high temperature}}\ \ \underset{}{5(Mg, Fe)_2SiO_4} + \underset{\text{plagioclase}}{NaCa_2Al_5Si_7O_{24}}$$

takes place at higher *P-T* conditions than does reaction (7). Hornblende, rhombic pyroxene, anorthite or olivine, garnet, and/or spinel can therefore coexist in equilibrium in unsaturated rocks in the *P-T* interval between reactions (7) and (8). Therefore hornblende occurs more commonly in basic than in acid rocks in the granulite facies or in the charnockite series of rocks. Another cause of the abundance of hornblende in the basic members of the charnockite series is that an increase of anorthite in the plagioclase will displace equation (7) toward the hornblende side (see below).

However, it is evident that even in silica-saturated rocks equation (7) is not closely restricted to a given curve in the *P-T* field because the minerals taking part in the reactions are mixed crystals (Ramberg, 1944*c*).

The composition of the plagioclase is

important. Because hornblende is observed to have a greater Ca/Na ratio than the coexisting plagioclase, it is evident that an increase of the Ca/Na ratio in the system displaces reaction (7) toward hornblende, stabilizing this mineral at rising temperatures. In the Greenland rocks the plagioclase appears to be rather uniformly near An_{35} (tables 1, 2), so that, in the rocks concerned, reaction (7) would not be affected much by changing composition of plagioclase.

The Mn-concentration in the garnets in reaction (7) is also important. Principally, increasing Mn/(Fe, Mg) ratio, which stabilizes garnet, will displace the equilibrium toward the garnet side and, consequently, also toward the hornblende side. However, in most of the Greenland rocks biotite and potash feldspar occur with garnet so that under equilibrium conditions the spessartite content is kept constant at the same *P-T*. In harmony with this theoretical conclusion the garnet analyses (tables 5 and 6) show very little differences in the MnO content. For the Greenland rocks, therefore, reaction (7) will not be disturbed by changing the Mn/(Fe, Mg) ratio in the garnets.

The $Mg/(Fe^{\cdot\cdot\cdot}, Fe^{\cdot\cdot})$ ratio is more varied in the rocks in question, as is the content of TiO_2. It now appears that the Fe members in equation (7) must react at somewhat higher *P-T* conditions than the pure Mg members. This is supported by the distribution of Mg and Fe between coexisting hornblendes and pyroxenes (tables 1, 2, 3, and 4). Consequently, changing of the Fe/Mg ratio will influence the equilibrium represented by equation (7).

Analyses and optical investigations show that common hornblende of the type $(Na, Ca)_{2-3}$ $(Mg, Fe, Al, Ti)_5$ $(Si, Al)_8O_{22}$ $(OH, F)_2$ is considerably richer in TiO_2 than the coexisting rhombic pyroxene (Groves, 1935, p. 158, and unpublished data on the Greenland rocks). This means again that increasing Ti/(Mg, Fe) ratio in the rocks stabilizes hornblende at continuously rising temperature. However, the hornblendes from the granulite facies area in Greenland show rather constant content of TiO_2 ranging from about 2.4 to 4.2 per cent

In conclusion, we can construct a subsolidus equilibrium diagram (fig. 3, *A*) showing how a varying $Mg/(Fe^{\cdot\cdot}, Fe^{\cdot\cdot\cdot})$ ratio influences the stability of hornblende and rhombic pyroxene in the boundary field between granulite and amphibolite facies. In this diagram the hornblende curve and the hypersthene curve will be displaced upward if the plagioclase is more basic than An_{40}, or the percentage of TiO_2 in hornblende exceeds about 3–4 per cent. The equilibrium curves will be displaced downward if the plagioclase becomes more acid than An_{30}.

Furthermore, the rocks investigated have intermediate to large Fe/Mg ratios (tables 1–4), so that the correctness of the Mg side of the diagram is not verified. For example, one would expect cordierite to appear together with garnet or to replace garnet completely where the Mg/Fe ratio exceeds a certain limit (Eskola, 1939; Folinsbee, 1941, p. 501). It is also very likely that the reaction point on the Mg side of the diagram (point *B*, fig. 3, *A*) is situated so low that enstatite is replaced by anthophyllite or cummingtonite. Thus, the following reaction probably takes place where the pure Mg members are present:

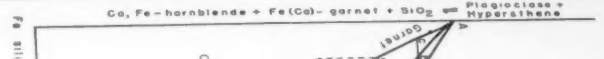
$$\underset{\text{quartz}}{3SiO_2} + \underset{\text{cordierite}}{Mg_2Al_4Si_5O_{18}} + \underset{\text{hornblende}}{NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2} \rightleftharpoons \underset{\text{anthophyllite}}{Mg_6Al_2Si_7O_{22}(OH)_2} + \underset{\text{plagioclase}}{NaCa_2Al_5Si_7O_{24}} \quad (9)$$

TABLE 1

QUARTZ-BEARING HORNBLENDE-ENDERBITIC GNEISSES FROM WESTERN GREENLAND*

		2,042	37,224	3,618	xHbg.	3,766	2,148	Hbg.4	Hbg.2	3,749	2,010	155	37,935	37,985	38,711
Plagioclase		An_{38}	An_{33}	An_{40}	An_{40}	An_{45}	An_{38}	An_{38}	An_{38}	An_{34}	An_{33}	An_{32}	An_{25}	An_{35}	An_{70}
Quartz		+	+	+	+	+	+	+	+	+	+	+	+	+	+
Potash feldspar		(+)	+	(+)	(+)	+	(+)	(+)	(+)	(+)	(+)	−	+	(+)	−
Rhombic pyroxene	γ	1.728	.....	1.720	1.718	1.723	1.717	1.727	1.720	.....	1.719	.....	.....	.....	1.689
	α	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
			−							+		−	−	+	
	Mg/Fe	58/48	.....	58/42	59/41	56/44	61/39	58/47	58/42	.....	59/41	.....	.....	.....	82/18
Monoclinic pyroxene	γ	1.723	.....	.....	1.716	.....	.....	1.723	.....	.....	.....	.....	.....	.....	.....
	α	.....	.....	1.693	.....	.....	.....	1.692	.....	1.687	.....	.....	.....	.....	.....
			−			+	−		−		−	+	−	−	−
Hornblende	γ	1.699	.....	1.693	1.692	1.690	1.690	1.693	1.692	1.677	.....	1.696	.....	1.700	1.652
	α	1.677	1.692	1.673	β: 1.684	.....	1.668	1.673	.....	1.657	.....	1.674	>1.698	1.678	1.632
											(+)				
	Mg/Fe	40/60	30/80	47/53	48/52	50/50	50/50	47/53	48/52	65/35	.....	43/57	.....	40/60	77/23
Biotite	β	.....	.....	.....	.....	.....	1.643	.....	.....	.....	1.643	.....	.....	.....	.....
	Mg/Fe	(+)	+	+	(+)	+	42/58	+	(+)	+	42/58	(+)	(+)	+	−
Garnet		−	+	+	−	−	−	−	−	−	−	−	+	−	−
Ilmenite and magnetite		+	+	+	+	+	+	+	+	+	+	+	+	(+)	(+)
Pyrite		−	−	−	(+)	−	−	−	+	+	+	+	+	+	(+)
Apatite		+	+	+	+	+	+	(+)	+	−	−	−	−	−	−
Sphene		−	−	−	−	−	−	−	−	−	−	−	+	−	−

* The relations between optical properties and chemical composition are taken from G. Kennedy, (1947); and S. Foslie, (1945). With reference to no. 38,711 it is doubtful that the rhombic pyroxene is stable in association with plagioclase. The Mg/Fe ratio in hornblende 38,711 is determined chemically.



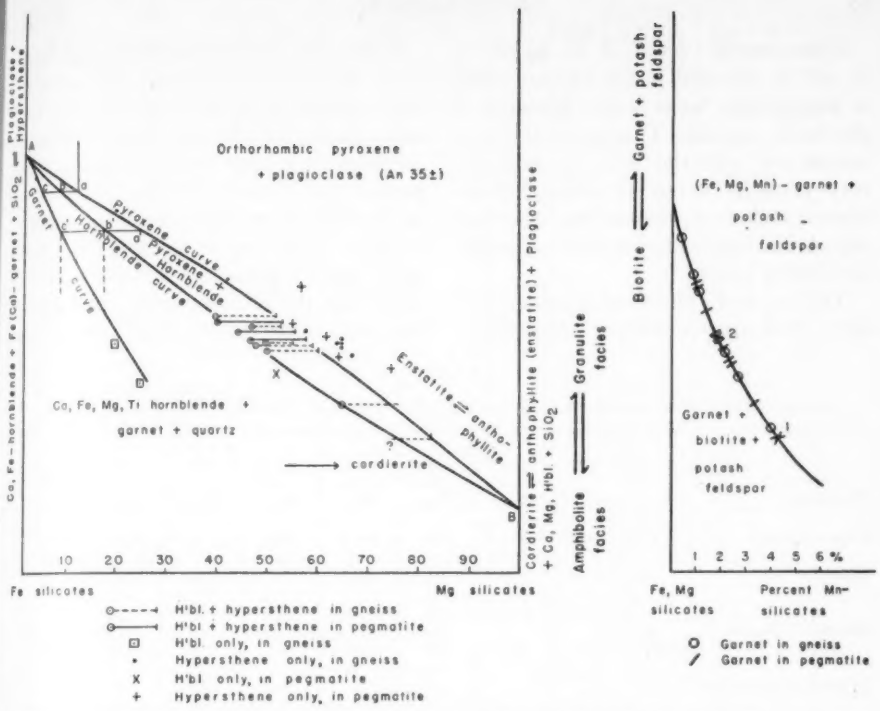


FIG. 3.—*A*, Subsolidus diagram of a saturated silicate system corresponding to composition given by equation (7), p. 36. The left-hand side of the diagram represents pure Fe components in this system, and the right-hand side represents pure Mg components in the same system. Point *A* corresponds to the transition point of the pure Fe members in equation (7), and point *B* to the transition point of equation (9).

Hornblende is unstable in the field: orthorhombic pyroxene $-An_{35}$. Rhombic pyroxene is unstable in the field: Ca, Fe, Mg, Ti-hornblende, garnet, quartz, cordierite. In the pyroxene-hornblende field are hornblende, rhombic pyroxene (and garnet plus plagioclase) in stable equilibrium.

Let us consider a paragenesis of An_{35} and hypersthene at decreasing temperature. At point *a*, for example, hypersthene begins to interact with plagioclase, forming hornblende of Mg/Fe ratio *b* and garnet of Mg/Fe ratio *c*. By decreasing temperature, the hypersthene follows the curve down to *a'*, the hornblende follows the curve down to *b'*, and garnet ends at *c'*. Now we suppose that at this point either hypersthene or plagioclase is completely used up in the reaction (eq. [7], p. 36) so that no more hornblende and garnet can form. Therefore, by further decrease in temperature, the composition of garnet and hornblende should be approximately constant following the stippled lines. (Because plagioclase is a mixed crystal, the last statement is not completely correct. However, a more thorough discussion is outside the aim of this paper.)

It should be noticed that the extremely Fe-rich and the most Mg-rich parts of the diagram are situated outside the actual composition of the investigated rocks. Nevertheless, the equilibrium curves are tentatively extended into these parts of the diagram. With reference to the Mg-rich part of the diagram we have some data which indicate that there is very little difference between the Mg/Fe ratios in hornblende and rhombic pyroxene.

B, This diagram represents the uppermost part of figure 2, *B*, thus being situated somewhat above the highest garnet marked in figure 2, *B*. The curve gives the spessartite content in garnets in equilibrium with biotite, ±sillimanite, and potash feldspar. All the garnets plotted are from the granulite facies area in western Greenland, tables 5 and 6. Point *1* represents garnet no. 37,817, table 6. Point *2* is the average per cent by weight of spessartite in the garnets from the granulite facies rocks.

Figures 3, *A*, and 3, *B*, are correlated to the transition interval between amphibolite facies and granulite facies and should therefore be easy to compare with figure 2, *B*.

Consequently, point *B* in figure 3, *A*, will be situated in the highest parts of amphibolite facies where enstatite is physically unstable. This would also harmonize best with the fact that cordierite very often is found in anthophyllite-bearing rocks but more seldom in regionally metamorphosed enstatite- or bronzite-bearing rocks.

Tables 1 and 2 give some mineralogical data from quartz-bearing hypersthene gneisses of the granulite facies area in western Greenland. According to the Mg/Fe ratio in the rhombic pyroxenes and the hornblendes in these rocks, they fall within a narrow *P-T* field in figure 3, *A*.

The MnO contents of garnets from some of the same gneisses and from khondalites, kinzigites, etc., in the same area are found in table 5 and plotted in the garnet-biotite equilibrium diagram, figure 3, *B*.

Table 3 shows some mineralogical data from the basic quartz-free rocks of the same district. It is seen that the Mg/Fe ratios in hornblende and rhombic pyroxene from these basic rocks are commonly greater than in the acid rocks. Thus, were we to place these minerals on the curves in figure 3, *A*, we would find that the basic rocks represent lower *P-T* conditions than the acid. However, in quartz-free rocks hornblende is stabilized owing to deficiency in SiO_2 (eqs. [7] and [8]), and the Mg/Fe ratio does not change with *P* and *T* in accordance with figure 3, *A*.

The hornblende-rhombic pyroxene assemblage in these basic rocks must be placed on the curves of figure 4. As is seen from the explanation of figure 4, the parageneses will in but few cases correspond to the olivine, hypersthene, enstatite, or hornblende curves where both olivine and plagioclase are present. Most of the mineral groups in table 3 are

TABLE 2

QUARTZ-BEARING HORNBLENDE-FREE ENDERBITIC GENEISSES FROM WESTERN GREENLAND

	2,144	2,007	3,833	2,401	5,000	2,019	158	Hbg. 30
Plagioclase	An_{26}	An_{38}	An_{33}	An_{38}	An_{33}	An_{48}	An_{10}	An_{25}
Potash feldspar	(+)	(+)	(+)	(+)	(+)	(+)	(+)	++
Quartz	+	+	+	+	+	+	+	+
Rhombic pyroxene γ	1.720	1.712	.....	1.712	1.712	1.717	.....	.....
Rhombic pyroxene α	.....	.....	1.700	.....	1.700	.....	1.696	1.728
Rhombic pyroxene Mg/Fe	58/42	65/35	64/36	65/35	65/35	61/39	67/33	42/58
Monoclinic pyroxene	+	−	−	−	−	+	−	+
Biotite β	.....	.....	.....	1.637	1.638	.....	.....	.....
Biotite Mg/Fe	+	−	−	50/50	50/50	+	+	(+)
Garnet	−	−	−	−	+	+	−	−
Ilmenite and magnetite	+	+	+	+	(+)	(+)	+	+
Pyrite	−	−	(+)	−	−	−	−	−
Apatite	+	+	+	+	+	(+)	+	+
Sphene	−	−	−	−	−	−	−	−

TABLE 3

QUARTZ-FREE GNEISSES FROM WESTERN GREENLAND

		Hypersthene-free Rocks			Hypersthene-bearing Rocks											
		3,739	2,038	2,075	2,188	2,074	2,016	2,129	3,310	Hbg.1	3,294	2,187	2,126	3,728	2,030	2,406	3,835
Plagioclase		An_{75}	An_{50}	An_{35}	An_{38}	An_{40}	An_{50}	An_{38}	An_{39}	An_{40}	An_{38}	An_{38}	An_{42}	An_{38}	–	An_{38}	An_{45}
Quartz		–	–	–	(+)	–	–	–	–	–	–	–	–	–	–	–	–
Potash feldspar		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Rhombic pyroxene	γ	.....	.....	.....	1.728	1.715	1.728	.....	1.711	.....	β: 1.700	.....	.....	1.711	β: 1.688	1.690	1.687
	α	.....	.....	.....	1.708	.....	.....	1.703	.....	1.700	.....	1.692	1.688	.....	.....	1.677	1.675
	Mg/Fe	–	–	–	55/45	62/38	52/48	62/38	66/34	64/36	71/29	70/30	74/26	66/34	78/22	82/18	83/17
Monoclinic pyroxene	γ	1.727	.....	.....	1.715	1.715	.....	1.720	.....	.....	1.716	.....	.....	1.711	1.713	.....	.....
	α	1.703	1.703	.....	.....	1.688	.....	1.695	.....	1.690	1.688	1.690	1.683	1.687	1.687	.....	1.677
				+			–		+							–	
Hornblende	γ	1.725	1.7105	1.692	β: 1.688	1.690	1.690	1.683	1.684	1.685	1.683	1.682	1.682	1.675	1.668	1.657	1.672
	α	1.703	1.6818	1.672	.....	1.670	1.665	1.657	1.664	1.660	.....	1.663	1.657	1.657	1.648	1.638	1.655
	Mg/Fe	?	46/54	47/53	40/60	50/50	53/47	62/38	58/42	59/41	60/40	60/40	62/38	67/33	74/26	?	89/11
Biotite	β	.....	.....	.....	1.655	.....	.....	.....	.....	1.645	1.635	1.638	.....	1.622	.....	.....	1.610
	Mg/Fe	–	–	+	30/70	–	–	+	+	45/55	50/50	48/52	+	60/40	–	+	70/30
Garnet		–	+	–	+	–	+	–	–	–	–	–	–	–	–	–	–
Olivine	γ	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.685	.....	1.680
	Mg/Fe	–	–	–	–	–	–	–	–	–	–	–	–	–	92/8	–	95/5
Ore		+	+	+	+	+	+	+	+	+	+	+	+	+	Spinel	+	+

TABLE 4

MINERAL ASSOCIATIONS OF HYPERSTHENE-HORNBLENDE–BEARING PEGMATITES AND "APLITES" FROM WESTERN GREENLAND

		PEGMATITES									"APLITES"		
		3,302	2,001	2,409	3,276	160	112	2,039	37,218	360	3,307	Hbg.6	2,002
Plagioclase		An_{33}	An_{40}	+	An_{40}	+	An_{32}	An_{60}	An_{40}	An_{36}	An_{38}	An_{32}	An_{38}
Quartz		+	+	+	+	+	(+)	(+)	+	+	+	+	+
Potash feldspar		+	+	+	+	+	+	(+)	(+)	(+)	+	+	+
Rhombic pyroxene	γ	1.713	1.719	1.715	.....	.....	1.723	1.699	Anal.	1.720	.....	.....	.....
	α	.....	.....	.....	.....	.....	.....	.....	+	.....	.....	1.699	.....
	Mg/Fe	$\frac{64}{36}$	$\frac{56}{42}$	$\frac{62}{38}$	(+)	−	$\frac{56}{44}$	$\frac{75}{25}$	$\frac{47.6}{52.4}$	$\frac{57}{43}$	+	$\frac{64}{36}$	+
Monoclinic pyroxene		−	−	−	−	(+)	−	−	+	−	+	α:1.687	+
Hornblende	γ	.....	.....	.....	1.700	1.692	.....	.....	.....	.....	.....	.....	.....
	α	.....	.....	.....	1.673	.....	.....	.....	.....	.....	.....	.....	.....
		−	+	−	.....	.....	−	−	Anal.	−	−	−	−
	Mg/Fe	.....	.....	.....	$\frac{40}{60}$	$\frac{45}{55}$	.....	.....	$\frac{44}{56}$	.....	.....	.....	.....
Biotite	β	.....	.....	.....	.....	.....	.....	1.625	.....	1.650	.....	.....	.....
	Mg/Fe	+	(+)	+	(+)	+	(+)	$\frac{60}{40}$	−	$\frac{40}{60}$	+	+	+
Ore		+	+	+	+	(−)	−	−	+	+	+	+	+
Apatite		+	(+)	(+)	(+)	+	−	+	(+)	(+)	+	+	+
Garnet		−	−	−	+	−	−	−	+	+	−	−	−

therefore situated between curve *Y* and the hornblende curve in figure 4. In this field hornblende and rhombic pyroxene exist in equilibrium, but only one or neither of the minerals olivine and plagioclase can be present.

We can conclude that the hornblende-hypersthene rocks of table 3 must lie within the same narrow *P-T* field as the assemblages of tables 1 and 2.

The harmony between field observation and mineralogical data from the granulite facies area in western Greenland is thus excellent; all data clearly show that the acid hypersthene gneisses and the garnet gneisses, as well as the basic noritic rocks, are formed or recrystallized at about the same pressures and temperatures.

Obviously, these different types of rocks did not crystallize out of a magma at the same *P-T* conditions. Such an as-

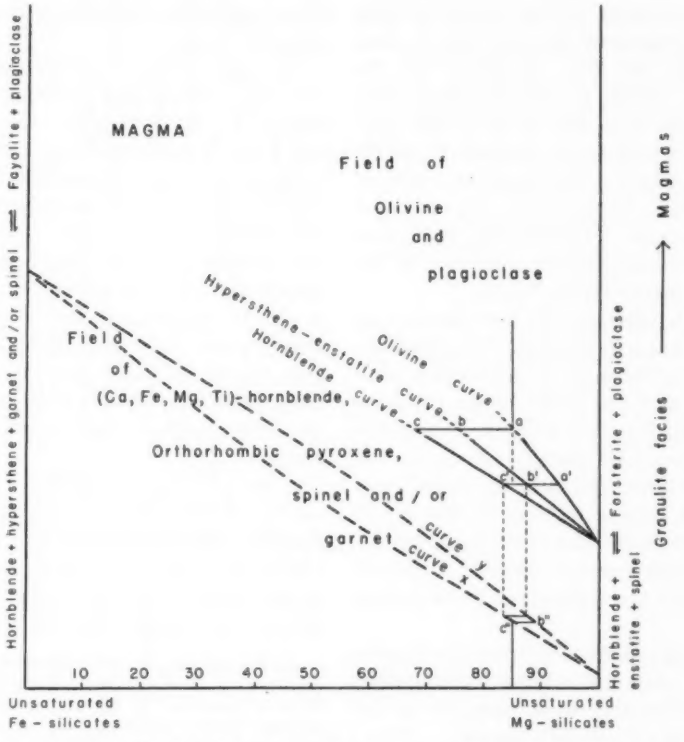


FIG. 4.—Approximate equilibrium diagram for systems represented by equation (8), p. 36, in which Fe and Mg are mutually substitutive. The pyroxene curve and the hornblende curve in figure 3, *A*, are stippled in figure 4 to correlate the two diagrams.

At point *a*, plagioclase begins to interact with olivine, forming hypersthene of composition *b* and hornblende of composition *c* (plus spinel). By decreasing temperature, olivine follows the curve down to *a'*, and rhombic pyroxene and hornblende follow the curves to *b'* and *c'*, respectively. At that point, plagioclase and/or olivine might be completely used up in the reaction. By further decreasing temperature, therefore, the composition of the hornblende and rhombic pyroxene does not change until curve *y* is reached. At lower temperatures, rhombic pyroxene will disappear.

sumption is contrary to basic thermodynamics as well as to the empirically established reaction series of Bowen.

Only in a restricted and unlikely case can we assume that the lowest-melting silicate system among the gneisses happened to be in a liquid state during the metamorphism of the complex and that this magma then crystallized simultaneously as the rest of the complex underwent metamorphism and acquired stable mineral facies. In other words, the solidus temperature of the lowest-melting silicate systems would have had to coincide with the *P-T* conditions of the granulite facies. It follows, under this hypothesis, that the cross-cutting pegmatites (which in the magmatic theory are supposed to crystallize later and at lower temperatures than the massifs) should contain mineral suites indicative of a lower temperature than that of the regional metamorphic facies.

In the hypersthene gneisses there occurs a very characteristic type of pegmatite marked by the same brownish-gray antiperthite as the massive gneiss, the same fine perthitic potash feldspar as found in the charnockitic variety of the gneiss, and commonly the same bluish-milky or brownish quartz as that of the hypersthene gneisses. Moreover, hypersthene, a brownish-green hornblende, garnet, and biotite are common in these pegmatites.

The pegmatites are, as a rule, connected with small-grained cross-cutting dikes also having the same minerals as the enderbitic-charnockitic gneiss.

The mineralogical data from the farsunditic or charnockitic pegmatites and "aplites," encountered in the hypersthene gneiss, are shown in table 4 and plotted in figure 3, *A*. These data can be interpreted only by assuming that the hypersthene-bearing pegmatites and "aplites" are formed at the same *P-T* conditions as the enclosing gneisses.

In some places a somewhat different type of pegmatite occurs in the hypersthene gneisses. Pink potash feldspar and grayish-white oligoclase are characteristic of these pegmatites, which have only biotite and/or garnet as ferromagnesian minerals. In such mineral suites the MnO content in garnet is the best temperature index. Nos. 361, 388, 37,580, and 37,976 in table 6 are of this type, showing that these pegmatites likewise belong to the granulite facies.

No hypersthene occurs in the numerous cross-cutting and conformable pegmatites in the kinzigites, khondalites, and other hypersthene-free rocks intermingled with the hypersthene gneisses. Garnet, however, is abundant in the last-mentioned pegmatites. To compare the mineral facies of these pegmatites with that of the gneiss complex, a series of MnO determinations were made. Tables 5 and 6 give the results and show that the investigated pegmatites inside the granulite facies area all belong to the same high facies as the country gneisses and massifs.[5]

Thus, with the help, first, of the critical mineral rhombic pyroxene; second, of the subsolidus equilibrium between hornblende and pyroxene; and, finally, of the garnet, potash feldspar $\rightleftarrows$ biotite equilibrium, it is shown that the mineral as-

[5] It is noteworthy that the hypersthene richest in iron (no. *xyz*, table 5) is associated with the most Mn-poor garnet (fig. 3). Likewise, it is in complete harmony with the theoretical considerations that the garnet no. 37,817, table 6, with the highest content of spessartite found inside the granulite facies area, belongs to a pegmatite occurring only a few hundred feet from the rock no. 38,711, table 1. This rock, which is situated in the boundary zone between granulite facies and amphibolite facies in Nagssugtoq, has a Mg-Fe distribution in its rhombic pyroxene and hornblende which places the paragenesis low in the hornblende—rhombic pyroxene diagram, figure 3, *A*.

TABLE 5

GARNET-BEARING GNIESSES FROM WESTERN GREENLAND*

	HOLSTEINSBORG			ISORTOQ		NAGSSUGTOQ				ARFERSIORFIK		NORTH OF AGTO
	3,286	2,188	2,024	37,547	*xyz*	37,612	37,887	37,787	37,847	37,390	37,380	37,935
Garnet % MnO % spessartite	1.16 2.69	0.85 1.97	0.4— 0.93	0.21 0.49	0.15 0.35	0.22 0.51	0.96 2.22	0.53 1.23	0.45 1.04	0.58 1.43	2.54 5.89	1.72 3.99 *n*: 1.799
Biotite β Mg/Fe	1.635 $\frac{5}{5}$	..... –	1.615 $\frac{7}{3}$	1.640 $\frac{5}{5}$	..... –	1.646 $\frac{4}{6}$	1.662 $\frac{2}{8}$	1.650 $\frac{4}{6}$	1.646 $\frac{4}{6}$	..... +	1.655 $\frac{3}{7}$	..... –
Plagioclase	+	+	+	+	+	+	+	+	+	+	+	+
Potash feldspar	+	–	+	(+)	(+)	(+)	+	–	+	–	–	+
Quartz	+	–	+	+	+	+	+	+	+	–	+	+
Others	Sillimanite	Hornblende Hypersthene Diopside	Sillimanite	Sillimanite	Hypersthene $\gamma \sim 1.77$ Fe/Mg = $\frac{80}{20}$	–	–	–	Cordierite	Cordierite	–	Hornblende Zircon Sphene

* All samples, except nos. 37,390 and 37,380, are from the granulite facies area (analysts: B. Bruun and H. Ramberg).

TABLE 6

GARNET-BEARING PEGMATITES FROM WESTERN GREENLAND*

	ISORTOQ							NAGSSUGTOQ					AGTO		ARFERSIORFIK			NORTH OF AGTO	
	361	342	343	388	37,512	37,580	360	37,738	37,718	37,817	37,848	37,857	37,976	37,218	37,364	37,381	37,423	37,878	37,449
Garnet																			
% MnO	0.50	0.75	0.61	0.44	0.95	1.07	0.39	0.79	0.43	1.83	0.73	0.51	0.99	0.82	1.43	7.38	20.0	4.46	3.66
% spessartite	1.16	1.74	1.41	1.02	2.20	2.48	0.91	1.83	1.00	4.25	1.69	1.13	2.29	1.92	3.32	17.12	46.0	10.35	8.49
n	.....	.....	1.788	.....	1.788	1.788	.....	1.788	1.783	.....	1.785	.....	1.783	.....	1.798	.....	.....	1.80	.....
Mg/Fe	.....	.....	$\frac{3}{7}$	.....	$\frac{3}{7}$	$\frac{3}{7}$	.....	$\frac{3}{7}$	$\frac{4}{6}$	.....	$\frac{3}{7}$	.....	$\frac{4}{6}$	.....	$\frac{25}{75}$	.....	.....	$\frac{25}{75}$	.....
Biotite β	.....	1.650	1.650	1.652	1.653	1.648	1.650	1.654	1.635	1.640	1.648	1.650	1.646	.....	1.646	.....	.....	1.670	.....
Mg/Fe	+	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{3}{7}$	$\frac{5}{5}$	$\frac{45}{55}$	$\frac{4}{6}$	$\frac{4}{6}$	$\frac{45}{55}$	–	$\frac{4}{6}$	+	–	$\frac{15}{85}$	–
Plagioclase	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Potash feldspar	+	+	+	+	+	+	(+)	+	+	+	+	+	+	(+)	+	+	+	+	+
Quartz	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Others	.....	.....	.....	.....	.....	.....	†	.....	.....	.....	.....	‡	.....	§	‖	.....	.....	.....	.....

* All samples are from the granulite facies area except nos. 37,381, 37,423, 37,878, and 37,449 (analyst: H. Ramberg).

† Rhombic pyroxene.

‡ Cordierite.

§ Hornblende, diopside, hypersthene. ‖ Sillimanite.

semblages of the pegmatites in the granulite facies in western Greenland are stable under granulite facies conditions. In addition, the comparatively low-temperature mineral muscovite, so commonly encountered in pegmatites in amphibolite facies areas, is found in only one of the hundreds of pegmatites examined. On the other hand, the high-temperature mineral sillimanite is encountered in some of the small conformable pegmatites penetrating the kinzigitic gneisses.

The chemical composition of these pegmatites in question exhibits considerable variation. No. 37,218, table 6, for example, is a plagioclase, hornblende, hypersthene, diopside, garnet, quartz, pegmatite with potash feldspar only in the form of antiperthite. No. 37,580, table 6, consists mostly of potash feldspar and quartz with garnet and biotite as the sole ferromagnesian minerals. No. 361 is a quartz vein with only small amounts of garnet, potash feldspar, and biotite. Therefore, the pegmatites in question cannot have the same melting interval; and, consequently, the only possible explanation is that they are formed during metamorphic-metasomatic processes below the solidus curve of silicate melts. Even without knowledge of the nature of these processes, it is evident that the granulite facies represents *P-T* conditions situated below the stability of "pegmatitic magma."

THE POSITION OF QUARTZO-FELDSPATHIC ROCKS IN THE MINERAL FACIES SCHEME

Unfortunately, no area has been studied from the viewpoint presented here, so it is difficult to compare the mineral facies of rocks and veins described in the literature. Therefore, let us first consider the facies classification of quartzo-feldspathic rocks, disregarding the degree of regional metamorphism in the area in which the rocks are situated.

For garnet-bearing quartzo-feldspathic rocks, the MnO content in the garnet is the most useful geothermometer. According to W. I. Wright (1938), the spessartite content in granite garnets ranges from almost 0 to 78.4 per cent and in pegmatite garnets from 1.4 to 90 per cent.

Placing these garnets in the equilibrium diagram, figure 2, *B*, we find that pegmatites and granites cover the same field of mineral facies ranging from low epidote-amphibolite facies up to granulite facies. (It has not been possible to determine whether the granite and pegmatite garnets of Wright's paper are in each instance in stable association with biotite. Some of the garnets may, therefore, have greater concentration of spessartite than that corresponding to the equilibrium curve in figure 2, *B*. This is true of the most spessartite-rich garnets recorded in Wright's paper.)

The epidote-plagioclase equilibrium in most quartzo-feldspathic rocks cannot register *P-T* conditions higher than those corresponding to An_{30-40} plus epidote, owing to the low Ca/Na ratio in these rocks. (Reference to Johannsen's descriptive petrography [1932, vol. 2] suffices to demonstrate that epidote or zoisite and An_{10-30} are commonly found in granodiorites, thus placing some of these rocks in epidote-amphibolite facies [fig. 2, *A*]).

In most pegmatites the Ca/Na ratio is still less than in massive rocks; therefore, the epidote-plagioclase equilibrium does not function, save below a rather low temperature limit. Examples of pegmatites with epidote and $An_{10\pm}$ are not rare (Andersen, 1931, p. 44; Erdmannsdörffer, 1931; and Wilkman, 1928).

Thus, the available data suggest that

most quartzo-feldspathic massifs and pegmatites exhibit mineral associations ranging from granulite facies down to epidote-amphibolite facies or actinolite greenschist facies. In other words, these rocks are formed and/or recrystallized below the field of magmatism.

Let us now briefly compare the mineral facies of various rocks and veins of areas outside the granulite facies.

AMPHIBOLITE FACIES AREAS

a) Some garnet-bearing pegmatites occur in the gneisses of the amphibolite facies north of the granulite facies complex in western Greenland. Nos. 37,449, 37,878, 37,423, and 37,381, table 6, are pegmatites from this area. No. 37,423 is a garnet replacing tourmaline in a biotite-free pegmatite. This garnet was formed, therefore, at higher temperature than that of the corresponding point on the equilibrium curve in figure 2, *B*.

Garnets from gneisses north of the granulite facies complex are shown in table 5, nos. 37,390 and 37,380. No. 37,935 is from the boundary zone between the granulite facies and the amphibolite facies. The rocks numbered 37,390 and 37,380 contain no potash feldspar, so the spessartite content in the garnets will be less than that corresponding to the equilibrium curve in figure 2, *B*.

However, the absence of hypersthene and sillimanite in this area shows that the gneisses around the pegmatites correspond to the amphibolite facies.

b) The Kantorp ore area in Sweden is worthy of special mention. According to Magnusson's (1936) description, the rocks have been formed and recrystallized under rather constant *P-T* conditions corresponding to the amphibolite facies. The index minerals are cordierite, sillimanite, andalusite, and anthophyllite. The highest *P-T* limit is indicated by the absence of hypersthene and the lower by the absence of epidote in spite of very basic plagioclase (up to An_{70}).

Table 7 shows the pertinent assemblages in the old gneisses, the younger granites, and the pegmatites in the Kantorp area. The whole complex, including

TABLE 7

Rock Types	Index Minerals from Rocks of Kantorp Area, Sweden*			Index Minerals from Rocks of Namaqualand, Africa†		
	Old Gneiss, Leptite	Younger Granites	Pegmatites	Old Gneiss	Younger Granites	Pegmatites
Plagioclase	An_{8-70}	$An_{25}\pm$	Oligoclase	Andesine	An_{10-43}	+
Potash feldspar	+	+	+	+	+	+
Biotite	+	+	+	+	+	+
Sillimanite	+	+	+	−	−	−
Andalusite	+	+	+	−	−	−
Cordierite	+	+	+	−	−	−
Garnet	+	+	+	−	−	Spessartite
Epidote	−	−	−	+	+	+
Chlorite	−	−	−	+	+	+
Muscovite	?	?	?	+	+	+
Hypersthene	−	−	−	−	−	−
Anthophyllite	(+)	−	−	−	−	−
Sphene	±	±	?	+	+	+

* After Magnusson. † After Coetzee; Gevers, Patridge, and Joubert.

both the conformable and the cross-cutting pegmatites, must have been formed at nearly the same *P-T* conditions, distinctly below the granulite facies, but well above the epidote-amphibolite facies.

c) Around Söndeled in southern Norway occur rocks belonging to the amphibolite facies and containing cordierite and anthophyllite but neither hypersthene nor epidote (Andersen, 1931, p. 43). Cross-cutting and conformable pegmatites carry the same index minerals (anthophyllite and cordierite) as the host gneisses.

d) A. Brammall and S. Bracewell (1936) have studied the garnets in the well-known Dartmoor granite. Muscovite, andalusite, and cordierite indicate approximately the facies. These minerals plus the absence of epidote place the granite in the amphibolite facies and distinctly below the granulite and pyroxene-hornfels facies.

Analyses of fourteen garnets from localities in the granite massif reveal great variation in manganese content, ranging from 3.3 per cent MnO (7.82 per cent by weight of spessartite) to 22 per cent MnO corresponding to 51 per cent spessartite. Thus, none of these garnets is so poor in spessartite as those from the rocks of the granulite facies in Greenland.

Brammall and Bracewell (1936) did not list the mineral associations of garnets with more than 7.3 per cent MnO, so the presence of biotite is in doubt. Therefore, it is not certain that the assemblages with the most spessartite-rich garnets actually represent as low temperatures as indicated by the Mn/(Fe, Mg) ratio. The garnets with 7.82–17 per cent by weight of spessartite are associated with both biotite and potash feldspar, making these garnets usable facies indicators for the Dartmoor granite. Probably the Dartmoor granite was formed, or recrystallized, at lower temperatures than the pegmatites from the granulite-facies area in Greenland.

Cordierite occurs with garnets of 7.30 per cent MnO (or 17 per cent spessartite), showing that cordierite is stable down to comparatively low temperatures.

EPIDOTE-AMPHIBOLITE FACIES AREAS

The literature contains insufficient data regarding this facies, so only a few examples can be considered.

a) South of the Orange River in Namaqualand in South Africa is an area of old gneisses and schists passing into younger granites to the south and east. The boundary between the old and young complexes is not sharp (Gevers, Patridge, and Joubert, 1937; Coetzee, 1941).

Coetzee's description shows that the old gneisses correspond partly to the highest epidote-amphibolite facies and partly to the lowest amphibolite facies. The younger granites to the south and east belong to a somewhat lower facies apparently not exceeding the highest boundary of the epidote-amphibolite facies. Table 7 shows the plagioclase-epidote associations in rocks described by Coetzee.

Whereas in western Greenland the gneissification and pegmatitization have taken place in the granulite facies, the activation in Namaqualand has taken place in the epidote-amphibolite facies and contains minerals consistent with this low-grade metamorphism. The Namaqualand pegmatites are not recorded as containing sillimanite, cordierite, or hypersthene but do carry muscovite and epidote (Gevers, Patridge, and Joubert, 1937).

The common garnet in the pegmatites is of rather constant composition, with the index of refraction ranging only from

1.815 to 1.820 and the density from 4.12 to 4.213 (Gevers, Patridge, and Joubert, 1937, p. 101). Analysis of one garnet shows 26.96 per cent MnO, corresponding to 61.55 per cent spessartite.

Placing this garnet in the equilibrium diagram, figure 2, *B*, reveals that it agrees closely with the epidote-plagioclase equilibrium of the host gneisses in the area.

b) In central Finland, east of Oulainen, many occurrences of unakite are reported (Wilkman, 1928). That the mineral assemblage of these masses belongs to the lowest epidote-amphibolite facies is indicated by the association of epidote and albite. In these rocks "primary" pegmatites are encountered with microcline, acid albite (An_{3-5}), epidote, quartz, chlorite, hematite, and apatite.

c) In the neighborhood of Notodden, in southern Norway, lies a body of epidote-oligoclase granite (Andersen, 1931, p. 44). Pegmatites in the granite contain epidote and acid plagioclase of nearly the same composition as the granite.

Andersen states that epidote was the first mineral to crystallize in the pegmatites, thus proving that epidote in this case cannot be interpreted as a "secondary" product.

d) At Weissenstein near Stammbach, Germany, occurs a zoisite-bearing pegmatite with plagioclase (An_{13-16}), muscovite, quartz, and some small garnets. According to O. H. Erdmannsdörffer (1931), the pegmatite is enclosed in a garnet-zoisite amphibolite with the same plagioclase as is found in the pegmatite.

e) Garnets from the pegmatites of southern Norway were investigated by the writer some years ago. The pegmatites are found in various rocks belonging to the epidote-amphibolite facies and to the amphibolite facies. The pegmatite garnets contain about 20–82 per cent by weight of spessartite. However, lack of samples of country rock associated with the pegmatites prevented direct comparison of the mineral facies.

CONCLUSIONS REGARDING THE FORMATION OF PEGMATITES

It is concluded that most pegmatites and quartzo-feldspathic masses in folded mountain zones were formed below the solidus curve of any magma. Furthermore, the pegmatites and most masses of quartzo-feldspathic composition have mineral assemblages of substantially the same facies as the country rocks. Therefore, it is concluded that most pegmatites and acid massifs in regional metamorphic areas were formed with the help of some submagmatic metamorphic-metasomatic processes.

Subsolidus formation of pegmatites and massifs takes place over a very wide *P-T* field: the epidote-amphibolite facies, the amphibolite facies, and the granulite facies. Only beyond the granulite facies at high pressure and in, or above, the pyroxene hornfels facies at low pressure can rock-making silicate melts exist. A discussion of the forces and kinetics underlying the metamorphic and metasomatic processes is not the aim of this paper.

Metasomatic-metamorphic pegmatites can be most conveniently classified into four groups:

1. *Secretion pegmatites* are formed by diffusion of atoms, molecules, and ions through the rocks toward open fissures and other places where mechanical pressure is low. Owing to the low mechanical pressure in such openings, the vapor tension of the minerals which grow here will also be low. Consequently, there exist forces which tend to make the activated movable atoms, ions, and molecules diffuse toward the openings where the ac-

tivated particles must consolidate into minerals.

2. *Concretion pegmatites* grow in solid rocks during regional metamorphism and push the country rocks in front of their expanding boundaries, thus developing a conformably stressed external contact zone. Because the mechanical pressure is high in the growing pegmatite and low in the surroundings, this type of petroblastic rock cannot be due to chemical potential differences induced by pressure differences. The driving agency here is the influence of the environment on the chemical potential or the vapor tension of the minerals. That is, feldspar and quartz intermingled with basic minerals should have a higher vapor tension than feldspar and quartz alone. Thus the diffusion processes tend to form concretions of more or less pure quartzo-feldspathic bodies.

3. Whereas in 1 and 2 the substances supplied might consolidate without reaction with old minerals in the space where the pegmatites form, *replacement pegmatites* are formed by intense reaction between introduced and pre-existing substances. The chemical potential differences necessary to form these pegmatites —to make the substances migrate toward the growing pegmatite and to make the activated particles consolidate— must be due to chemical incompatibility between the pre-existing minerals and the surrounding rocks.

4. *Recrystallization pegmatites* are formed by coarse-grained metamorphic recrystallization within limited spaces in the rocks. Pegmatites formed in this way will have almost the same chemical and mineralogical composition as the enclosing gneisses. The conformable cordierite-garnet pegmatites in kinzigitic gneisses are supposed to belong to this type.

Pegmatites are commonly of quartzo-feldspathic composition regardless of the composition of the country rocks. This is not because a quartz-feldspar system has the lowest melting temperature but because the elementary constituents of quartz, potash feldspar, and acid plagioclase are able to diffuse more readily than the constituents of most basic minerals. However, basic constituents can diffuse to some degree, and, therefore, the minor minerals in pegmatites (biotite, garnet, diopside, hornblende, cordierite, and several of the rare minerals) actually depend on the type and composition of the country rocks.

Only where the country rock is very poor in potash, soda, silica, etc., and the sources of these substances are distant will the pegmatites have a nonquartzo-feldspathic composition. Good examples are the corundum-bearing pegmatites found in ultrabasic rocks in the northern Transvaal (Brandt, 1946).

The chemical interrelation between pegmatites and the country rocks requires much more investigation. One interesting point is that many pegmatites can be classified according to content of *groups* of elements. Thus the Li pegmatites are rich not only in Li but also in other typical elements accompanying Li, such as Sn and F. This grouping of elements seems to be easily explained if it is assumed that the substances are introduced as liquid solutions or silicate melts charged with the typical group of elements required.

However, if the elements migrate in the form of individual atoms, molecules, or ions, a certain interdependence and grouping of the elements must also be expected. The principal reason is that migrating atoms, ions, or simple molecules cannot usually consolidate into crystalline elements or simple molecules in the pegmatites. The vapor pressure of

such crystalline elements or simple molecular compounds is so high that the elements will tend strongly to combine into more complicated compounds having lower partial vapor pressure of their several constituents. Thus, owing to chemical forces, certain groups of elements will tend to consolidate in pegmatites despite the more or less independent migration of these elements toward the growing pegmatite. In micas, for example, there is a relationship between the content of Li and the F/OH ratio so that Li-rich micas tend to be rich in F^- and poor in OH^- because of interionic polarization forces.[6]

In two hypothetical rock complexes, assume the same small concentration of Li_2O but different concentrations of F. In both complexes pegmatites form during metamorphism. It is likely that the pegmatites growing in the F-rich rocks will favor the formation of Li micas, whereas Li does not find conditions favorable for consolidation into Li minerals in the pegmatites forming in the F-poor complex.

Similarly, if both rock complexes contain traces of Sn, cassiterite will most likely form in the Li pegmatites in the F-rich complex but not in the pegmatites in the F-free complex. This is because the volatile SnF_4 molecules will diffuse more easily intergranularly than individual Sn atoms, ions, or less volatile Sn compounds.[7]

Because we must doubt the magmatic origin of most pegmatites and even the importance of circulating pore solutions in metamorphic-metasomatic rocks, we have to look for forces and processes of the kinds indicated above in our speculations about the formation of pegmatites and other bodies of quartzo-feldspathic composition.[8]

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[6] According to oral communication from Dr. F. Wickman.

[7] On field and experimental evidences as well as on theoretical grounds the writer considers it unlikely that large-scale diffusion through solid rocks preferably takes place through the silicate lattices. Many large atoms or ions (K, F, etc.), and also molecules such as H_2O, CO_2, etc., are much more mobile than are small ions or atoms. Furthermore, it can be shown that the mobility of the several particles in rocks increases with rising partial vapor pressure of the particles. It seems very probable that large-scale migration through solid rocks takes place with the help of "gaseous" atoms and molecules adhered to the mineral surfaces or the mosaic fissures. Only to a considerably less extent will lattice diffusion extend over large distances.

[8] After this paper was sent to press, garnets from two new pegmatites from the amphibolite and epidote-amphibolite facies areas in western Greenland were analyzed. No. 36647 contains 12.45 per cent MnO; No. 12020 contains 19.22 per cent MnO.

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FREQUENCY DISTRIBUTION OF THE MINERALS IN TWO PETROGRAPHIC PROVINCES[1]

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ABSTRACT

The frequency distribution of the major rock-forming minerals in the Oslo petrographic province and in the intra-Pacific province has been determined. In a concluding section several ways to arrive at the average mineral composition of igneous rocks are presented for consideration.

INTRODUCTION

Petrographers have noticed as a significant and striking fact that, although more than a thousand minerals are known, the number that composes over 99 per cent of igneous and metamorphic rocks is very small. Indeed, minerals that are really essential in rock-forming processes number somewhat less than a score, depending upon how strictly each mineral species is defined.

Recent trends in petrography have been toward quantitative calculations; although numerous detailed rock descriptions, including modes, have been published, no quantitative information on the regional frequency distribution of the several minerals is available.

In this paper mineral data on the igneous rocks of the Oslo province and of the intra-Pacific province are presented and statistically treated. Petrochemical studies of these provinces, published long ago, should be consulted for detailed descriptions (Clarke and Washington, 1924; Daly, 1944; Barth, 1931 and 1945; Macdonald, 1946 and 1947).

METHODS OF CALCULATION

A quantitative mineral determination in a rock can be made with a microscope and an integrating stage. This is known as the "Rosiwal analysis." The process is often tiresome and may require specially prepared thin-sections. The recalculation of chemical data is more convenient if large numbers of chemical analyses are available from a rock province.

In such calculations molecular (or atomic) proportions must be used. Here I want to repeat my old plea to all petrographers that the results also be stated in terms of molecules. There is no special significance attached to the weight of a mineral, and I see no reason whatsoever for converting the molecular proportions into weight percentages. The chemical relations of a rock are obscured by the use of weight percentages; moreover, the computations become unnecessarily cumbersome.

It seems nonsensical to me that Billings and Rabbitt (1947) should write:

> Although the use of molecular proportions greatly facilitates the calculations, it is less precise than it would be to assign the oxides by weights per cent. . . . Niggli (1936) and Barth (1945) have advocated using atomic percentages in all petrographic calculations. Whatever the advantages of Niggli's system, the "slack" is even greater than in the method employing molecular proportions.

This statement is equivalent to saying that, although the use of the metric system facilitates most calculations,

[1] Manuscript received June 7, 1948.

measurements taken with a meter stick are less precise than those taken with a yardstick. Furthermore, Billings and Rabbitt, as well as everybody else who wants to present a rock analysis in terms of mineral molecules, use molecular (or atomic) proportions as one step in the procedure. The results thus obtained cannot possibly become more accurate by being restated in terms of weight percentages.

The fundamental question, stripped of all formalities, is whether or not it is possible to calculate the mineral composition with no other knowledge than the chemical analysis of an igneous rock. The answer, in the general case, is that it is not possible. There are many reasons for this, the most important probably being that the crystallization (or recrystallization) of most rocks took place under changing P-T conditions which prevented establishment of equilibrium among the minerals; zoned feldspars, armored relics, and glass attest to disequilibria. Obviously, therefore, the mineral composition cannot be regarded as a one-valued function of the chemical composition, even within a defined mineral facies. Nevertheless, in most rocks the approach to equilibrium has limited the possibilities of variation in the mineral assemblages to such an extent that, with some additional information, accurate results can be obtained.

In most cases it will be necessary to know the chemical composition or the amount of one or more of the minerals present. Still, there is no automatic approach, as in the case of the norm calculations; but trial-and-error methods must be employed. It becomes of great importance, therefore, to use a quick and simple method of computation; otherwise the expenditure of time becomes prohibitive. The best method for this purpose is that proposed by Niggli in 1936.

TABLE 1

CALCULATION OF THE MINERAL CONTENTS OF AN OSLO-ESSEXITE FROM RANDVIKSHOLMEN

	Si	Ti	Al	$Fe^{'''}$	$Fe^{''}$	Mg	Ca	Na	K	P	Sum
ATOM PER CENT OF ROCK	45.7	1.4	14.4	5.2	6.6	8.1	9.4	6.7	2.1	0.4	100.0
Alkali feldspar ($Or_{60}Ab_{40}$)	7.5	.....	2.5	.....	.....	.....	.....	1.0	1.5	.....	12.5
Plagioclase (An_{34})	20.5	.....	10.3	.....	.....	.....	2.6	5.1	.....	.....	38.5
Pyroxene	15.5	0.9	1.4	1.2	2.9	6.4	6.0	0.6	0.2	.....	35.1
Olivine (Fa_{33})	1.1	.....	.....	.....	0.7	1.5	.....	.....	.....	.....	3.3
Biotite	1.1	0.1	0.2	0.4	0.7	0.2	.....	.....	0.4	.....	3.1
Ore	.....	0.4	.....	3.6	2.2	.....	.....	.....	.....	.....	6.2
Apatite	.....	.....	.....	.....	.....	.....	0.6	.....	.....	0.4	1.0
Sum	45.7	1.4	14.4	5.2	6.5	8.1	9.2	6.7	2.1	0.4	99.7

In petrographic calculations it has been customary to use the proportions of the molecules, such as SiO_2, Al_2O_3, etc. Niggli recommended the use of the proportions of the several cations (silicon and metals); recalculated to 100, they represented what Niggli called the "equivalent molecular percentages" which form the basis for the calculation of the mineral molecules (table 1). It should be noticed that in this scheme the molecular amount of a mineral becomes propor-

tional to the sum of the cations in the mineral. In this way the mineral equations become very simple, for instance:

$$NaAlSiO_4 + 2SiO_2 = NaAlSi_3O_8$$
$$3Ne + 2Q = 5Ab$$

(the nepheline formula contains three cations, the quartz one cation, and the albite five cations).

An example of this calculation of the mineral composition of an alkali gabbro is given in table 1. In this case the chemical composition of the constituent pyroxene was known (and the nature of the feldspars was determined optically). In other cases, if no mineral analysis was available, the amounts of one or several of the minor minerals were determined by Rosiwal analyses. In no cases do the calculations become wholly automatic, however; recourse must be had to trial-and-error methods. Nevertheless, the results are very reliable. One cannot fail to become impressed by the fact that a few simple and routine observations with the microscope usually limit the possibilities so much that the results are very nearly correct. For further details, the reader is referred to the previous papers by Niggli and Barth, cited above.

THE OSLO PETROGRAPHIC PROVINCE

Through the classical works of the last century by Kjerulf and Brögger, the Oslo area became one of the best-known rock provinces. The Oslo plutonics form a mildly alkaline series, ranging from alkali gabbro through syenite (and nepheline syenite) into ægerite granite (and biotite granite). Brögger regarded these rocks as comagmatic and genetically related to the corresponding lavas. The areal distribution of the principal rock types in the Oslo province is listed in table 2, which is quoted from an earlier publication (Barth, 1945).

The same paper contains data for the quantitative mineral composition of sixty-four plutonic igneous rocks. Additional data are found in papers by Sæther (1945) and by Oftedahl (1946). These data are treated here statistically, and the results are exhibited in tables 3–9.

TABLE 2

AREAL DISTRIBUTION OF THE PRINCIPAL ROCK TYPES IN THE OSLO PROVINCE

Rock Type	Km.²	Per Cent
Oslo-essexite	15.3	0.3
Akerite	52.2	1.0
Kjelsasite (= mica syenite, in part)	201.0	4.0
Lardalite (= nepheline syenite)	65.0	1.3
Larvikite (= augite syenite)	1670.0	32.8
Nordmarkite-pulaskite	1425.0	28.0
Ekerite (= soda granite)	821.0	16.1
Biotite granite	840.0	16.5
Plutonic rocks	5089.5	100.0
Basaltic lava	220.0	15.6
Rhomb porphyry	1160.0	82.2
Quartz porphyry	30.6	2.2
Extrusive rocks	1410.6	100.0
	6500.1	.....

THE INTRA-PACIFIC ROCK PROVINCE

The rocks of the intra-Pacific islands are preponderantly of basaltic habit, with small amounts (*ca.* 3–5 per cent) of alkaline lavas, mostly trachytes and phonolites. The mean mineral composition of these two rock groups is shown in table 10. The rocks are well known both chemically and mineralogically (Macdonald, 1947); detailed petrographic descriptions, including modes calculated in weight per cent, have been given for sixty rock specimens (Barth, 1931). These investigations form the basis of the present statistical studies.

If we assume the relative areal distribution of basaltic rocks, on the one side, and phonolite-trachytic rocks, on the other, to be 95 per cent and 5 per cent, respectively,[2] the average mineral composition of the whole petrographic province comes out as shown in column III, table 10.

TABLE 3

AVERAGE MINERAL COMPOSITION OF ESSEXITES AND BASALTS

	I*	II†
Plagioclase	40	47
Augite	23	20
Hornblende	8.5	10
Alkali feldspar	7.5	8
Ores	7.5	8
Biotite	5.5	.....
Olivine	3.0	.....
Serpentine	2.0	2
Apatite	1.0	.....
Sphene	0.5	0.5
Calcite	0.5	1
Quartz	0.4	1
Chlorite	0.3	2
Hypersthene	0.2	.....
Muscovite	0.1	.....
Epidote	.....	0.2
Glass	.....	0.2
Zeolite	.....	0.1
Total	100.0	100.0

* Twenty Oslo-essexites. † Four Oslo-basalts.

TABLE 4

AVERAGE MINERAL COMPOSITION OF KJELSASITES AND AKERITES

	I*	II†
Plagioclase	42.0	39
Alkali feldspar	28.5	35
Quartz	6.0	6
Augite	6.0	2
Hornblende	6.0	10
Ores	5.0	3
Biotite	3.0	3
Apatite	2.0	0.7
Serpentine	0.8	1
Olivine	0.4	.....
Hypersthene	0.3	.....
Sphene	0.03	0.3
Calcite	0.03	.....
Total	100.06	100.0

* Seven kjelasites. † Ten akerites.

COMPARISONS AND CONCLUSIONS

It stands to reason that the average mineral composition of the whole intra-Pacific province cannot be much different from that of the Hawaiian rocks.

Daly (1944) has computed the average chemical composition of a "primary oli-

TABLE 5

AVERAGE MINERAL COMPOSITION OF TWO LARDALITES

Aklaki feldspar	54
Nepheline	16
Ores	10
Pyroxene	7
Biotite	5
Olivine	4
Apatite	2.5
Sodalite	1.0
Hornblende	0.5
Total	100.0

TABLE 6

AVERAGE MINERAL COMPOSITION OF LARVIKITES, RHOMB PORPHYRIES, AND NORDMARKITES

	I*	II†	III‡
Alkali feldspar	45.5	60	87
Plagioclase	34.0	25	.....
Augite	7.5	2	1
Hornblende	2.5	.....	3
Ores	2.5	1	2
Quartz	2.0	3	2
Biotite	2.0	.....	2
Pyroxene	1.0§	.....	1.5‖
Olivine	0.9	.....	.....
Apatite	0.9	0.5	0.4
Nepheline	0.7	.....	.....
Sphene	0.4	.....	1
Calcite	0.1	2	0.1
Chlorite	.....	5	.....
Muscovite	.....	1	.....
Epidote	.....	0.5	.....
Total	100.0	100.0	100.0

* Seven larvikites
† Sixteen rhomb porphyries.
‡ Eight nordmarkites.
§ Hypersthene.
‖ Ægerite.

[2] This may be an overestimation of the amounts of alkaline lavas; but, if one takes only half this amount, the results will not be notably changed.

TABLE 7

AVERAGE MINERAL COMPOSITION OF EKERITES, GRANITES, AND QUARTZ PORPHYRIES

	I*	II†	III‡
Alkali feldspar	73.5	70.5	60.0
Quartz	18.5	26.0	36.0
Ægerite	4.5	.....	.....
Ores	1.2	1.5	1.5
Biotite	.....	0.7	1.0
Plagioclase	.....	.....	0.5
Sphene	1.0	0.4	0.4
Hornblende	1.0	0.3	0.2
Chlorite	.....	0.3	0.3
Apatite	0.1	0.2	0.1
Zircon	0.1	.....	.....
Fluorite	0.1	0.1	.....
Total	100.0	100.0	100.0

* Six ekerites. In the ekerites, elpidite and astrophyllite are present in amounts less than 0.1 per cent.

† Four granites.

‡ Two quartz porphyries.

TABLE 8

WEIGHTED AVERAGE MINERAL COMPOSITION OF OSLO ROCKS

	I*	II†
Alkali feldspar	52	65
Plagioclase	28	13
Quartz	3	9
Pyroxene	5	5‡
Chlorite	4	.....
Ores	2	2
Hornblende	2	2
Calcite	2	.....
Biotite	.....	2
Muscovite	0.8	.....
Apatite	0.4	0.6
Epidote	0.3	.....
Olivine	0.3§	0.4
Sphene	0.1	0.6
Nepheline	.....	0.4
Inclusive	0.1‖	¶
Total	100.0	100.0

* All extrusive rocks.

† All plutonic rocks.

‡ Including 1.5 per cent ægerite, 0.3 per cent hypersthene, 3.2 per cent augite.

§ Serpentine.

‖ Present in amounts <0.1 per cent: glass, biotite, zeolite.

¶ Present in amounts <0.1 per cent: chlorite, serpentine, calcite; <0.01 per cent: fluorite, sodalite, zircon, astrophyllite, elpidite.

TABLE 9*

WEIGHTED AVERAGE MINERAL COMPOSITION OF ALL OSLO ERUPTIVE ROCKS (86 ANALYSES)

(Surface Area = 6500 Km.²)

Aklaki feldspar	62
Plagioclase	16
Quartz	8
Pyroxene	5
Hornblende	2
Ores	2
Biotite	2
Chlorite	0.8
Sphene	0.5
Apatite	0.5
Calcite	0.4
Nepheline	0.3
Olivine	0.3
Muscovite	0.2
Total	100.0

* Present in amounts <0.1 per cent: serpentine and epidote; <0.01 per cent: fluorite, sodalite, zircon, glass, zeolite, astrophyllite, and elpidite.

TABLE 10

AVERAGE MINERAL COMPOSITION OF PACIFIC ROCKS

	I*	II†	III‡
Alkali feldspar	10	61	13
Plagioclase	31	18	30
Pyroxene	28	6§	27
Olivine	10	0.2	9.5
Ores	7.5	5	7.4
Glass	7.7	2	7.4
Hornblende	.....	2	0.1
Quartz	1.0	2.5‖	1.1
Nepheline	2.3	1.6¶	2.2
Apatite	1.2	0.6	1.2
Serpentine, etc.	0.5	0.5	0.4
Biotite	.....	0.5	.....
Inclusive	0.8	0.1	0.7**
Total	100.0	100.0	100.0

* Fifty rocks of basaltic habit; includes twenty-seven olivine basalts, twelve basalts, five pacificites, five tephrites and basanites, and one trachybasalt.

† Two phonolites + two trachytes + one rhyolite.

‡ All Pacific lavas.

§ Including 1.4 per cent acmite.

‖ Including 0.6 per cent tridymite.

¶ Including 0.5 per cent analcite.

** Present in amounts less than 0.1 per cent are biotite, tridymite, cristobalite, epidote, prehnite, calcite, melilite, sodalite, noselite, hauyne, sphene, zircon, kaolinite, sulfur, and sulfates.

vine basalt," which he regards as the material out of which all the lavas of Hawaii have been made, and for the most part without contamination. However, some of the alkaline lavas (nepheline basalt, etc.), he believes, were formed through reaction with carbonate rocks.

If the primary olivine basalt represents the mother magma, then it should

TABLE 11

MINERAL COMPOSITION OF PACIFIC LAVAS

	I*	II†	III‡
Alkali feldspar	18	9	15
Plagioclase	30	40	34
Pyroxene	27	34	26.5
Olivine	9.5	5.7	10.5
Ores	7.4	6.6	6.1
Quartz	3.5	3.5	3.5
Nepheline	2.2	0.0	2.7
All others	2.4	1.2	1.7
Total	100.0	100.0	100.0

* Average mineral composition of all Pacific lavas, quoted from column I, table 10. The glass which is present to the amount of 7.4 per cent in the Pacific lavas has, for comparison purposes, been recalculated into 2.4 per cent quartz and 5 per cent alkali feldspar.

† Computed mineral composition of Daly's "primary olivine basalt."

‡ Computed mineral composition of all Hawaiian lavas from Washington's average chemical analysis.

be capable of producing a mineral assemblage similar to that listed in column III, table 10, for the Pacific province.

Table 11 shows that Daly's primary olivine basalt magma cannot produce such a mineral assemblage: alkali feldspars are too low, plagioclases are too high, and, if quartz is to correspond to the amounts in which it is actually observed, then the computed amounts of the undersaturated minerals (olivine and nepheline) become too low.

This is what one would expect; for Daly believes that some of the "alkaline" rocks of Hawaii were formed through assimilation of limestone, the obvious result of which will be to increase the amounts of olivine and nepheline.[3]

Instead of Daly's primary magma, we will, therefore, consider the average chemical composition of all Hawaiian lavas, as determined by Washington, in which he took the average of all good analyses of such lavas. This average analysis can be recalculated into a mineral assemblage which comes very close to the one observed for the Pacific province (table 11).

The mineral calculations referred to above can be checked easily by the data displayed in table 12. The assumptions involved are that the pyroxene phases contain small amounts of Ti, Al, and ferric iron (from 0.5 to 2 per cent), and the composition of the alkali feldspar is 40 Or, 60 Ab.

There are no accurate data on record of the average mineral composition of

TABLE 12

CHEMICAL ANALYSES STATED IN TERMS OF PERCENTAGES OF THE CONSTITUENT CATIONS

	I*	II†	III‡
Si	47.0	46.4	55.8
Ti	2.2	1.9	0.8
Al	14.9	15.0	17.1
Fe^{+3}	1.9	2.0	2.2
$Mn^{+2}+Fe^{+2}$	7.2	6.8	3.0
Mg	10.9	11.5	4.9
Ca	10.6	9.1	5.1
Na	4.4	5.7	7.1
K	0.7	1.2	3.8
P	0.2	0.4	0.2
Total	100.0	100.0	100.0

* Primary olivine basalt of Hawaii (Daly's average).

† All lavas of Hawaii (Washington's average).

‡ All igneous rocks (Clarke and Washington's average).

igneous rocks; but much thought has been given to the chemical composition. By taking the average of all good analyses, Clarke and Washington (1924)

[3] But not of alkali feldspar. Therefore, the writer believes in a more alkaline primary magma rather than in limestone syntexis.

have arrived at figures which are generally believed to represent the average chemical composition of all igneous rocks. This analysis is included in table 12.

If we want to compute the mineral composition corresponding to this average analysis, assumptions must be made as to the average abundance of undersaturated minerals (nepheline and olivine). Because Clarke did not include the extensive areas of the ocean floors in his average, it would seem that the amounts of olivine and nepheline must be rather small. We can follow Leith and Mead (1915) and put the amount of olivine as 2.6 per cent. Nepheline will be taken, quite arbitrarily, as 0.3 per cent.

In column I, table 13, the result of this computation is given. The composition of the alkali feldspar is supposed to be Or:Ab = 1:1.

Column II gives the average mineral composition of a mixture of intra-Pacific lavas and granite in the ratio 1:1. This corresponds to a mixture of the two dominant rock provinces in the earth. For the average granite the data given by Larsen (1942) were used.

Column III corresponds to the composition of the average igneous rock as computed by Leith and Mead (1915) by taking 65 per cent granite and 35 per cent basalt.

Column IV contains a "rough estimate" of the mean mineral composition of the igneous rocks as a result of a statistical examination of about seven hundred such rocks by Clarke and Washington (1924).

TABLE 13*

AVERAGE COMPOSITION OF IGNEOUS ROCKS

	I	II	III	IV
Quartz	12.4	14	20.4	12.0
Alkali feldspar	31.0	29	50.2	59.5
Plagioclase	29.2	28		
Pyroxene	12.0	13.5	12.9	16.8
Hornblende	1.7	0.5	1.6	
Biotite	3.8	2.5	3.9	3.8
Muscovite	1.4	(0.4†)	3.8	
Olivine	2.6	4.8	2.6	
Nepheline	0.3	1.1	.....	
Ores	4.1	5.2	4.6	
Chlorite and serpentine	0.6	(0.2†)	.....	7.9
Apatite	0.6	(0.6†)	.....	
Titanite	0.3	(0.2†)	.....	
Total	100.0	100.0	100.0	100.0

* Explanation of figures in columns given in text.

† Larsen gives no figures for these minerals in his average granite.

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OXIDATION AND REDUCTION IN GEOCHEMISTRY[1]

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ABSTRACT

Because many elements can occur in two or more oxidation states, reactions involving oxidation and reduction are important in geochemical processes. The energy change per equivalent of a reaction involving oxidation and reduction can be quantitatively expressed by its oxidation potential. For many inorganic reactions taking place in aqueous solution oxidation potentials are known and can be used to obtain a better understanding of geochemical processes. Conditions within the earth's crust may vary from highly oxidizing to highly reducing, and the oxidation potential of a natural environment determines what minerals may or may not be formed in that environment. The solution, transportation, and deposition of many elements in the earth's crust are strongly influenced by the oxidation potential of the environment. Separation of closely related elements, such as iron, cobalt, and nickel, may result. The significance of oxidation potentials in geochemistry is particularly marked in the frequent concentration and enrichment of rare elements in deposits formed under extreme oxidizing or reducing conditions.

INTRODUCTION

Many elements may occur in different oxidation states in the earth's crust. Commonest of such elements is iron, which occurs as the native metal (oxidation state 0), as ferrous compounds (oxidation state 2), and as ferric compounds (oxidation state 3). Similar elements are manganese (2, 3, 4), sulphur (−2, 0, 6), chromium (3, 6), vanadium (3, 4, 5), copper (0, 1, 2), cobalt (2, 3), lead (0, 2, 4), arsenic (0, 3, 5), antimony (0, 3, 5), silver (0, 1), nitrogen (−3, 0, 5), iodine (−1, 5), and many others. The concept of oxidation, which originally meant the addition of oxygen to a substance, now implies simply the increase in the oxidation-state number of an element, or, expressed in terms of the electronic theory for ionic compounds, the loss of electrons by an atom; reduction is, of course, the reverse process.

The stability of an element in a particular oxidation state depends upon the energy change involved in adding or removing electrons to transform it into a higher or lower oxidation state. Given a quantitative measure of this energy change for different reactions involving oxidations and reductions, it is then possible to arrange these reactions in order of intensity. Such a quantitative measure is provided by the factor known variously as the "oxidation-reduction potential," "oxidation potential," or "redox potential"; throughout this paper it will be referred to as the "oxidation potential." The concept of oxidation potential can be visualized in the following way: Consider a solution containing equal concentrations of the ions of the reduced and oxidized form of some element (e.g., ferrous and ferric iron), in which is immersed an unattackable electrode; a certain potential will be set up in that electrode, depending upon the tendency of the reduced form to give up electrons to the electrode and thereby transform to the oxidized form. The potential thus set up is the oxidation potential of the reaction by which the reduced form is transformed to the oxidized form and is signified by E_o. The oxidation potential of any reaction is a relative figure, the standard of reference being the reaction

$$H_2 = 2H^+ + 2e \qquad (e = \text{electron})$$

(i.e., the removal of electrons from hydrogen atoms or the oxidation of hydro-

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gen to hydrogen ions). The oxidation potential of this reaction, for unit concentration[2] of the reacting substances (E_o), is arbitrarily fixed as 0.00 volt, and the scale of oxidation potentials extends on either side of zero.

Reactions involving oxidation and reduction can thus be rated according to intensity by their oxidation potentials. A positive value for an oxidation potential means that the oxidized form of the couple is a stronger oxidizing agent than hydrogen ions are and that the reduced form is a weaker reducing agent than is gaseous hydrogen; a negative value implies that the oxidized form is a weaker oxidizing agent than hydrogen ions are and that the reduced form is a stronger reducing agent than is gaseous hydrogen. The extreme values on the scale of oxidation potentials are for the following reactions:

$$2HF = F_2 + 2H^+ + 2e\ , \quad E_0 = 3.03 \text{ volts};$$
$$Cs = Cs^+ + e\ , \quad E_0 = -3.02 \text{ volts}.$$

In other words, gaseous fluorine is the strongest oxidizing agent known, and metallic cesium the strongest reducing agent. For positive values of E_o, reactions tend to go from right to left, for negative values of E_o, from left to right.

Table 1 lists a few of the many reactions whose oxidation potentials are known, in order of decreasing oxidation potential, i.e., in order of increasing reducing power, the reduced form of any couple having sufficient energy to reduce the oxidized form of any couple of higher positive potential.

The E_o values are for the reactions at 25° C. when all the substances involved are at unit activity. The potential at other activities and temperatures is given by the expression

$$E = E_0 + \frac{RT}{nF} \ln Q$$

where Q is the product of the activities of the resultants divided by the product of the activities of the reactants, each activity raised to that power whose exponent is the coefficient of the substance in the reaction; ln signifies natural logarithms ($\ln x = 2.3026 \log x$); R is the gas constant (8.3151 volt coulombs); T is the absolute temperature; F is a faraday of electricity (96,500 coulombs); and n is the number of electrons involved in the reaction as written. This expression reduces to

$$E = E_0 + \frac{0.0002T}{n} \log Q$$

At 25° C. (298° absolute),

$$E = E_0 + \frac{0.06}{n} \log Q$$

The direct influence of temperature on oxidation potential is therefore very slight; for $n = 1$ and $\log Q = 1$ and with a change of temperature of 100° C., this would amount to only 0.02 volt. The indirect effect of temperature in changing the activities of the substances involved in the reaction would probably outweigh its direct influence. Variations in concentrations (activities) of the reacting substances do, however, have a marked effect on the oxidation potential of the reaction. For example, in the reaction

$$Fe^{2+} = Fe^{3+} + e\ , \quad E_0 = 0.77 \text{ volt},$$

if Fe^{3+}/Fe^{2+} is 100/1, then E will be 0.89 volt; and if Fe^{3+}/Fe^{2+} is 1/100, E will be 0.65 volt. This variation of oxidation potential with the concentration is of special importance in reactions involving hydrogen or hydroxyl ions, as many

[2] More correctly, "unit activity," activity being a function of concentration which provides for deviation from the laws of perfect solutions.

oxidation-reduction reactions do (table 1). In aqueous solutions, hydrogen-ion concentrations may vary from unity to 10^{-14} or, expressed in terms of pH, have pH from 0 to 14. Such a variation produces large changes in oxidation potentials involving hydrogen or hydroxyl ions and must be taken into account in applying E_o values to actual reactions. The influence of pH on the oxidation potentials of some reactions given in table 1 is shown graphically in figure 1.

The oxidation potential of a reaction gives information only about the state of chemical equilibrium and not about the rate at which this equilibrium is attained. The oxidation potential is a measure of the energy change involved in the reaction; but, even if the reaction is one which takes place with a decrease of free energy, it does not mean that the reaction will necessarily proceed at a significant rate under given conditions. For instance, the mechanism of the reaction may be such that it cannot take place in spite of a favorable potential value. Thus $Fe = Fe^{3+} + 3e$, $E_o = -0.04$ volt indicates that H^+ should oxidize iron to the ferric state; but the mechanism of the reaction is $Fe = Fe^{2+} + 2e$, $E_o = -0.44$ volt, and $Fe^{2+} = Fe^{3+} + e$, $E_o = 0.77$ volt and H^+ cannot bring about the second step. In general, it may be stated that many reactions for which oxidation

TABLE 1

	E_o (in Volts)
$Co^{2+} = Co^{3+} + e$	1.84
$Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e$	1.75
$Au = Au^+ + e$	1.68
$Mn^{2+} = Mn^{3+} + e$	1.51
$Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e$	1.46
$Cr^{3+} + 4H_2O = HCrO_4^- + 7H^+ + 3e$	1.3
$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e$	1.28
$2H_2O = O_2 + 4H^+ + 4e$	1.23
$VO^{2+} + 2H_2O = HVO_3 + 3H^+ + e$	1.1
$I^- + 3H_2O = IO_3^- + 6H^+ + 6e$	1.09
$VO^{2+} + 3H_2O = V(OH)_4^+ + 2H^+ + e$	1.00
$NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e$	0.84
$Ag = Ag^+ + e$	0.80
$Fe^{2+} = Fe^{3+} + e$	0.77
$Ni(OH)_2 + 2OH^- = NiO_2 + 2H_2O + 2e$	0.49
$U^{4+} + 2H_2O = UO_2^{2+} + 4H^+ + 2e$	0.41
$4OH^- = O_2 + 2H_2O + 4e$	0.40
$Cu = Cu^{2+} + 2e$	0.34
$V^{3+} + H_2O = VO^{2+} + 2H^+ + e$	0.31
$I^- + 6OH^- = IO_3^- + 3H_2O + 6e$	0.26
$PbO + 2OH^- = PbO_2 + H_2O + 2e$	0.25
$Co(OH)_2 + OH^- = Co(OH)_3 + e$	0.2
$H_2S = S + 2H^+ + 2e$	0.14
$H_2 = 2H^+ + 2e$	0.00
$NH_3 + 9OH^- = NO_3^- + 6H_2O + 8e$	−0.12
$Cr(OH)_3 + 5OH^- = CrO_4^{2-} + 4H_2O + 3e$	−0.12
$Pb = Pb^{2+} + 2e$	−0.13
$Sn = Sn^{2+} + 2e$	−0.14
$Mn(OH)_2 + OH^- = Mn(OH)_3 + e$	−0.40
$Fe = Fe^{2+} + 2e$	−0.44
$S^{2-} = S + 2e$	−0.51
$Fe(OH)_2 + OH^- = Fe(OH)_3 + e$	−0.56
$Pb + 2OH^- = PbO + H_2O + 2e$	−0.58
$Zn = Zn^{2+} + 2e$	−0.76

potentials have been calculated are not capable of experimental attainment under equilibrium conditions for one of two reasons: (*a*) the rate of the reaction is exceedingly slow, or (*b*) the final and initial substances cannot exist together because of an intermediate state, as, for example, the Fe–Fe^{3+} couple instanced above.

THE OXIDATION POTENTIAL OF NATURAL ENVIRONMENTS

Before proceeding to the discussion of the application of oxidation potentials to specific geological and geochemical problems, it is desirable to consider in some detail the factors controlling the intensity of oxidizing and reducing processes which take place in nature. Brief consideration will make clear the fact that many reactions for which oxidation potentials are given in the literature never take place in natural environments (for example, the oxidation of sulphate to persulphate or the reduction of titanium compounds to metallic titanium). This indicates that the range of oxidation potentials of natural environments is limited, thereby limiting the reactions which may or may not take place.

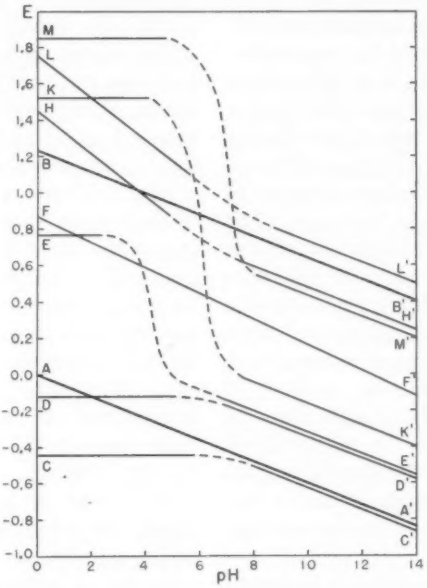

FIG. 1.—Variation of oxidation potential with pH for certain reactions

A. $H_2 = 2H^+ + 2e$
B. $2H_2O = O_2 + 4H^+ + 4e$
C. $Fe = Fe^{2+} + 2e$
D. $Pb = Pb^{2+} + 2e$
E. $Fe^{2+} = Fe^{3+} + e$
F. $NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e$
H. $Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e$
K. $Mn^{2+} = Mn^{3+} + e$
L. $Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e$
M. $Co^{2+} = Co^{3+} + e$

A'. $H_2 + 2OH^- = 2H_2O + 2e$
B'. $4OH^- = O_2 + 2H_2O + 4e$
C'. $Fe + 2OH^- = Fe(OH)_2 + 2e$
D'. $Pb + 2OH^- = PbO + H_2O + 2e$
E'. $Fe(OH)_2 + OH^- = Fe(OH)_3 + e$
F'. $NH_3 + 9OH^- = NO_3^- + 6H_2O + 8e$
H'. $PbO + 2OH^- = PbO_2 + H_2O + 2e$
K'. $Mn(OH)_2 + OH^- = Mn(OH)_3 + e$
L'. $Ni(OH)_2 + 2OH^- = NiO_2 + 2H_2O + 2e$
M'. $Co(OH)_2 + OH^- = Co(OH)_3 + e$

This limitation is due to the fact that chemical reactions at or near the earth's surface take place, in general, in aqueous solution. Theoretically, this limits the reactions which can occur to those with oxidation potentials lying between those for the reactions

$$H_2O = \tfrac{1}{2}O_2 + 2H^+ + 2e\,,\ E_0 = 1.23 \text{ volts}\,,$$

and

$$2H^+ + 2e = H_2\,, \qquad E_0 = 0.00 \text{ volt}\,.$$

The oxidized form of any couple with a higher potential than that for the first reaction will theoretically decompose water with the evolution of oxygen and hence cannot be formed in aqueous solution. The reduced form of any couple with a lower potential than that for the second reaction will theoretically decompose water with the evolution of hydrogen and similarly cannot be formed in aqueous solution. It is found that the theoretical requirements are not strictly met in practice, on account of overvoltage phenomena, i.e., it requires a greater potential than the theoretical to produce the evolution of hydrogen or oxygen at a measurable rate. However, a study of the reactions actually taking place in nature indicates that the potentials of these two reactions do largely control the nature of the oxidations and reductions that take place under natural conditions.

Both these reactions involve hydrogen ions, and their potentials are thus strongly affected by changes in hydrogen-ion concentration. The E_0 values given above are, of course, for hydrogen-ion concentrations of unity, i.e., pH = 0, and the potentials decrease (at 25° C.) 0.06 volt for each tenfold decrease in hydrogen-ion concentration (each unit increase in pH). The pH of natural waters is very variable, ranging from as low as 0 in strongly acid waters of volcanic regions to 10 or more in alkaline areas where sodium carbonate is present in solution. As a rule, however, the pH of natural waters lies between 4 and 9, the great majority being within one unit of the figure for pure water (pH = 7). For a pH of 7 the potential of the first reaction would be 0.82 volt and of the second reaction would be −0.41. This gives a range of 1.23 volts, compared to the total range of the scale of oxidation potentials of about 6 volts; therefore but a comparatively small number of oxidation-reduction reactions may be expected to take place under natural conditions.

The above figures indicate that the oxidation potentials of natural environments, where the pH is near 7, should lie between −0.41 and 0.82 volts. Unfortunately, comparatively few measurements of the oxidation potentials of natural environments have been made. ZoBell (1946) has made a number of measurements of oxidation potentials in recent marine sediments on the California coast and obtained values ranging from 0.350 (in sandy deposits from shallow, well-oxygenated water) to −0.500 volt (in fine-grained bottom deposits rich in organic matter), the pH ranging from 6.4 to 9.5. Allgeier, Hafford, and Juday (1941) found the oxidation potentials of surface waters in Wisconsin lakes to be 0.38–0.50 volt, of bottom water 0.057–0.44, and of bottom sediments, −0.14–0.2. Hutchinson, Deevey, and Wollack (1939), also investigating lake waters, found potentials of 0.4–0.5 volt in surface waters, and potentials as low as 0.10 in bottom waters. These rather meager data in general fall well within the limits predicted by the foregoing theoretical discussion. It will be noted, however, that in fine-grained bottom deposits rich

in organic matter ZoBell found potentials as low as −0.500 volt, more negative than the theoretical potential of −0.42 volt required to liberate hydrogen from water at pH 7. ZoBell ascribes this creation of a hydrogen overvoltage to the presence of anaerobic bacteria, which thrive in such environments.

It would be interesting to have more measurements of the oxidation potentials of natural waters, particularly from more unusual environments, such as desert areas, where conditions are extremely oxidizing, and from mineral springs and mine waters. Because these measurements can readily be made with the same equipment as that used extensively for the electrometric measurement of pH, it is not too much to hope that, where measurements of pH of natural waters are being made, measurements of oxidation potential will be made at the same time.

A study of mineral associations enables predictions to be made regarding the approximate oxidation potential under which the minerals were formed. The rare occurrence of metallic iron in carbonaceous sediments indicates an extremely low oxidation potential at the time of formation. Another strongly reducing environment must have been that which gave rise to the association of native lead and pyrochroite [$Mn(OH)_2$] found in veins in the mine at Långban, Sweden. Ferrous compounds are generally considered as indicative of strongly reducing conditions, but reference to figure 1 shows that, in strongly acid solutions, ferrous iron is not readily oxidized to the ferric state. At the other end of the scale the occurence of minerals containing chromate, nitrate, or iodate or of plattnerite (PbO_2) or stainierite (CoOOH) indicates strongly oxidizing conditions of origin.

APPLICATION OF OXIDATION POTENTIALS TO GEOCHEMICAL PROBLEMS

The concept of oxidation potentials is capable of wide application in geochemistry, as the solution, transportation, and deposition of those elements which may occur in two or more oxidation states are directly and powerfully influenced by the oxidation potential of the environment. The application of oxidation potentials to geochemical problems was first discussed by Goldschmidt (1933) and more recently by Scerbina (1939), Mason (1941), and Chapman and Schweitzer (1947).

THE OCCURRENCE OF NATIVE ELEMENTS

The occurrence or nonoccurrence of elements in the native state is readily explained on the basis of oxidation potentials. The higher the potential required to remove electrons from a metal and convert it into metallic ions, the greater the tendency for the metal to be found in the native state. On the other hand, if an element has an oxidation potential lower than that of the hydrogen electrode, it is theoretically impossible to discharge its ions in aqueous solution, so that it can be formed only in a nonaqueous environment. Observations on the occurrence of native metals bear out these contentions. Gold and platinum, which have oxidation potentials greater than 1 volt, occur almost entirely as native metals. Copper, silver, and mercury, which have oxidation potentials between 0 and 1 volt, are found both as native metals and in compounds. Metals with negative oxidation potentials occur native very rarely and have evidently been formed under special circumstances. Native lead has been found at a number of localities; its oxidation potential is only slightly negative (−0.13 volt), and reference to figure 1 shows that in alkaline

and weakly acid solutions its oxidation potential is greater than that of the hydrogen electrode and therefore it could be deposited from such solutions. Tin, with an oxidation potential of −0.14 volt, has also been reported in the native state. Most of the terrestrial occurrences of native iron are in igneous rocks; but it has been found in carbonaceous sediments. The negative oxidation potential of −0.44 volt for iron would at first seem to preclude the deposition of native iron from aqueous solutions; but reference to figure 1 reveals that, on account of the rapid decrease in the potential of the hydrogen electrode with increase of pH and of the overvoltage required to discharge hydrogen ions, iron could be deposited from solutions of low hydrogen-ion concentration; the oxidation potential of −0.500 volt recorded by ZoBell (1946) for a marine mud indicates that under suitable conditions metallic iron could be produced in such an environment. The only element with oxidation potential lower than that of iron which has been recorded as occurring in the native state is zinc (−0.76 volt). All records of native zinc are extremely dubious, and the reported native zinc is probably of artificial origin. Of the many elements with oxidation potentials less than that of zinc—the alkali and alkaline-earth metals, aluminum, titanium, chromium, manganese—none is known to occur native.

STEPWISE OXIDATION OF IRON-MANGANESE MINERALS

The oxidation of minerals containing both iron and manganese affords an interesting example of the influence of oxidation potentials on mineral formation. There are a number of phosphate minerals containing both divalent iron and manganese—triphyllite, lithiophilite, natrophilite, arrojadite, and graftonite; they alter readily and are remarkable for the number and diversity of their alteration products. They all show a typical stepwise alteration, characterized by the complete oxidation of the iron to the trivalent state before the divalent manganese is affected. This alteration gives rise to a number of mineral species—sicklerite, alluaudite, landesite, salmonsite, etc.—containing divalent manganese and trivalent iron. The oxidation potential required to convert ferrous to ferric iron is so much lower than that required to convert divalent manganese to the trivalent or tetravalent state that the oxidation of the ferrous iron proceeds to completion before the manganese is affected.

Incidentally, it is interesting to note that a much higher potential (1.51 volts) is required to convert manganous ions into manganic ions than is required to convert manganous ions into manganese dioxide (1.28 volts). Furthermore, the latter potential decreases rapidly with increase in pH, whereas the former is independent of pH, at least in solutions sufficiently acid to prevent the precipitation of hydroxides. This accounts for the rarity of compounds containing trivalent manganese as minerals; under normal conditions oxidation of manganous compounds results in the formation of pyrolusite and psilomelane. The formation of purpurite [$(Mn,Fe)PO_4$] by the oxidation of the phosphate minerals mentioned above suggests that the presence of phosphate ion greatly reduces the normal potential required to oxidize manganous to manganic ions, probably on account of complex formation between manganic and phosphate ions.

CONDITIONS OF FORMATION AND STABILITY OF MINERALS

The oxidation potential of the environment is an important factor in the

formation of minerals, and therefore from the nature of a mineral association it is often possible to ascertain the conditions of paragenesis. Reverting to the occurrence of native lead at Långban in Sweden mentioned previously, the native lead occurs associated with pyrochroite [$Mn(OH)_2$] in veins which were evidently formed at comparatively low temperatures from aqueous solutions. Study of figure 1 shows that the oxidation potential of the medium must have been negative to permit deposition of metallic lead and that deposition probably took place in an alkaline or only weakly acid solution, because in strongly acid solution the oxidation potential of lead is less than that of the hydrogen electrode. The alkaline nature of the medium is confirmed by the occurrence of pyrochroite, as the precipitation of $Mn(OH)_2$ requires a pH of 8 or greater.

Similarly, the high potentials required to convert divalent cobalt to trivalent cobalt and divalent lead to PbO_2 in acid solution indicate that the minerals stainierite (CoOOH) and plattnerite (PbO_2) are deposited from alkaline solutions, for which the oxidation potentials are much less (fig. 1). Figure 1 shows that for many reactions the oxidation potentials decrease rapidly with the increase of pH, generally more rapidly than does the corresponding decrease in the oxygen and hydrogen electrodes. Thus oxidation in general proceeds more readily, the more alkaline the solution. The potentials for some oxidations in alkaline solutions, particularly those which result in the precipitation of practically insoluble compounds, lie far below the potentials for corresponding oxidations in acid solutions. This is especially marked with respect to the oxidation of ferrous to ferric iron; in acid solution the potential is 0.77 volt and is not affected by pH; however, as soon as the pH increases to a figure at which ferric hydroxide is precipitated (about pH 2–3) the oxidation potential drops sharply to a negative figure. Thus ferrous salts are comparatively stable in acid solution, being only slowly oxidized by air; but in solutions sufficiently low in acid for $Fe(OH)_3$ to be precipitated, oxidation proceeds rapidly to completion. Deposition of ferrous compounds in nature therefore demands either a very acid environment or one with a very low oxidation potential, on the negative side of zero.

SEPARATION OF ELEMENTS ON THE BASIS OF OXIDATION POTENTIALS

The separation of closely related elements in the upper zone of the lithosphere by processes involving solution and redeposition is often brought about by their distinctive properties with respect to oxidation and reduction.

A very good example is that of the three elements iron, nickel, and cobalt. Generally they occur together in primary deposits, yet supergene processes result in their separation. Figure 1 shows that these three elements differ greatly in the potentials required to oxidize them beyond the divalent state. Iron is readily oxidized to the trivalent state in alkaline and mildly acid environments; cobalt requires a much higher potential even in alkaline solution, and in acid solutions the potential required lies high above that for the oxygen electrode; nickel does not form trivalent compounds, but a dioxide is known, the formation of which, even in alkaline solutions, requires potentials somewhat higher than that for the oxygen electrode. This is reflected in natural occurrences: the common form of iron in supergene deposits is as hydrated ferric oxide; hydrated cobaltic oxide (stainierite) is found only where conditions have been strongly oxidizing; and the higher oxide of nickel is not known to

occur as a mineral. The separation of these three elements by supergene processes is well illustrated in New Caledonia, where serpentinized ultra-basics altering under tropical conditions give rise to lateritic material rich in Fe_2O_3 and concentration of nickel as garnierite and of the cobalt as pockets of hydrated cobaltic oxide. In this connection the work of Leith and Mead (1916) on the lateritic iron ores of eastern Cuba is pertinent. On the basis of chemical analyses of the residual iron ore and of the serpentine from which it was derived, they showed that, in contrast to the enrichment in iron in the residual deposit, the nickel and the cobalt are strongly decreased in absolute amount and even more strongly in relative amount; these two elements have evidently been largely removed in solution on account of their greater stability in the divalent state.

Oxidation processes also result in a similar separation of manganese and iron. Manganese is often closely associated with iron in primary deposits, the ferrous and the manganous ions being similar in their chemical nature. Supergene processes, however, generally lead to a complete separation of iron from manganese; because the potential required to convert iron to the ferric state is so much lower than that required to convert manganese to manganese dioxide, the iron is readily precipitated as hydrated ferric oxide, whereas the manganese remains in solution and is eventually deposited under more oxidizing conditions as comparatively iron-free manganese dioxide.

ENRICHMENT OF RARE ELEMENTS IN OXIDIZING OR REDUCING ENVIRONMENTS

It has been observed that rare elements are often concentrated by natural processes in unusual environments. These environments are often characterized by very high or very low oxidation potentials. A good example is the marked concentration of iodine in the highly oxidizing environment of the nitrate deposits of northern Chile, the iodine having been fixed in the form of iodates. The ores of copper, lead, vanadium, and uranium which are found in sandstones and shales far from igneous rocks, generally represent deposits formed under desert conditions in oxidizing environments; these deposits often show marked concentrations of rarer elements also, especially silver, nickel, cobalt, chromium, molybdenum, and selenium. Analyses of natural deposits of manganese dioxide, in the form of pyrolusite and psilomelane, frequently show notable amounts of rarer elements, especially cobalt, copper, and molybdenum, sometimes also lead and tungsten. At the other end of the scale, in highly reducing environments, rarer elements are also enriched. Such reducing environments are the present-day black marine muds rich in organic matter and anaerobic bacteria and, on land, areas of accumulation of decaying vegetable matter, such as peat swamps. In the geological column these are represented by bituminous and carbonaceous shales. Goldschmidt (1935) found in coal ash marked concentration of cobalt, nickel, gallium, germanium, molybdenum, and arsenic. In this connection the frequent association of millerite (NiS) with coal is noteworthy. Similarly, the ash of natural hydrocarbons generally shows considerable amounts of vanadium and often also of nickel and molybdenum. The Mansfeld copper slate in Germany, probably a "fossil" black marine mud, is an example of a bituminous shale which is worked for its copper content and which also shows notable concentration of vanadium, arsenic, antimony,

molybdenum, cadmium, silver, gold, and metals of the platinum group (Cissarz and Moritz, 1933). It is not clear to what extent the original concentration of rare elements in these reducing environments took place as a result of the vital activities of plants and animals or during subsequent processes of decay and mineralization, but in any case the fixation of these rare elements was largely controlled by the strongly reducing conditions prevailing in these sediments.

Such concentrations of rare elements suggest that sedimentary deposits formed under strongly oxidizing or reducing conditions deserve careful examination for unexpected concentrations of rare elements, which under favorable circumstances may be present in workable amount, either alone or as a by-product of the exploitation of some common ore. In this connection sedimentary manganese deposits represent a commonly occurring environment of high oxidation potential, and carbonaceous and bituminous shales an environment of low oxidation potential. Such materials may eventually prove to be important sources of these rare elements whose industrial importance is continually growing.

THE OXIDATION POTENTIAL OF NONAQUEOUS ENVIRONMENTS

The theory and applications of oxidation potentials have been developed from a consideration of reactions taking place in aqueous solutions, and practically no progress has yet been made toward applying the theory to reactions taking place in nonaqueous environments. Because most reactions taking place in the upper zone of the lithosphere undoubtedly are "wet," the utility of this theoretical background in a consideration of these reactions is very great. Nevertheless, the broad field of magmatic reactions cannot be attacked satisfactorily at present because oxidation potentials determined in aqueous solutions at room temperatures can hardly be extrapolated to the high temperatures and otherwise very different conditions of a silicate melt. Yet reactions involving oxidation and reduction undoubtedly take place in magmas. All magmas contain iron and hydrogen and oxygen in some form, and reactions involving equilibria between divalent and trivalent iron and between hydrogen, oxygen, and water must play a large part in determining the minerals which are produced on crystallization. In general, the magmatic environment is a reducing environment, as in minerals formed by direct magmatic crystallization the elements are generally present in the lowest oxidation state in which they occur in nature. In plutonic rocks, especially the more basic, ferrous iron is commonly predominant over ferric iron, and even in volcanic rocks, which have had greater opportunity to acquire oxygen, the same relation generally holds. Titanium may be present in igneous rocks to some extent in the trivalent state; the violet color and pleochroism of titanium-bearing augite is suggestive of the Ti^{3+} ion. Incidentally, the most reducing environment represented in nature is probably that of meteorites, which contain metallic iron, oldhamite (CaS), and daubreelite (Cr_2FeS_4). There is undoubtedly a wide and interesting field in the investigation of oxidation and reduction in a magmatic environment, but experimental difficulties are great and the theory largely undeveloped.

OXIDATION AND REDUCTION IN THE GEOCHEMICAL CYCLE

The geochemical cycle in the lithosphere can be conceived as proceeding from the initial crystallization of a mag-

ma through the alteration and weathering of the igneous rock; the transportation and deposition of the material thus produced; then the cycle continues through diagenesis and lithification to metamorphism of successively higher grade until eventually, by processes of anatexis and palingenesis, a magma is regenerated. Like any ideal cycle, the geochemical cycle may not be realized in practice; the cycle may be indefinitely halted at some stage, or its direction may be reversed; but nevertheless it provides a useful concept to serve as a basis for discussion of many aspects of geochemistry.

The processes of oxidation and reduction are distinctly correlated with different stages in the geochemical cycle outlined above. As previously pointed out, the magmatic environment is a strongly reducing one, and rocks formed by direct magmatic consolidation generally show a low oxidation state. Alteration and weathering take place at or near the earth's surface, where the presence of free oxygen produces a high oxidation potential; and in this part of the cycle the highest oxidation state is reached. Diagenesis and lithification may result in some degree of reduction, especially in sediments rich in organic matter; and metamorphism, especially in its higher grades, quite generally results in progressive reduction until finally the material is brought back to its originally magmatic condition. Nevertheless, the imprint produced on the material by oxidation at the earth's surface may persist throughout the metamorphic part of the cycle, and often a high state of oxidation of a metamorphic rock (which may be most readily recognized by a high Fe_2O_3/FeO ratio) is a useful indication of the original sedimentary character of the rock.

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CELLULAR STRUCTURES IN GLASS AS RELATED TO STRUCTURES IN LAVA[1]

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ABSTRACT

Cellular structures which form during the cooling of some unusual optical glasses are described. These resemble in several respects ellipsoidal structures in lava. The former are shaped by convection currents present in the cooling liquid and remain visible in the chilled material because of chemical and physical differentiation of the liquid. It is suggested that some of the structures in lava variously called ellipsoidal, pillow, or globular may have formed by convection flow modified by horizontal movement of the lava stream and followed by rather rapid quenching.

GENERAL STATEMENT

The origin of structures which may develop in a body while changing from a fluid to a solid has long been an interesting subject of discussion (Bénard, 1900; Dauzère, 1908; Lewis, 1914; Sosman, 1916; Foye, 1924; Fuller, 1931; and Stark, 1938). The structures occurring commonly in basalt, called ellipsoidal, pillow, or globular, are generally assumed to have formed during extrusion into water, the rapid chilling of the lava being a condition of their formation. Columnar or prismatic structures in lavas no doubt usually result from contraction of the layer during cooling, but formation of columnar structures chiefly as a result of convection flow of the fluid lava during cooling is a possible explanation for some occurrences of this structure (Longchambon, 1913; Sosman, 1916, p. 223).

The writer recently had the opportunity of studying structures which form during the cooling of some optical glasses.[2] These structures resemble in some respects those occurring in lavas; and inasmuch as there is little doubt as to the general mechanism of their formation, it has seemed worth while to describe them.

DESCRIPTION OF STRUCTURES

Examples of cellular structures in glass are shown in plate 1 and figures 1 and 2. In plate 1, *C*, is shown a typical specimen exhibiting cellular structure. The composition of the mixture was such that, on cooling, the glass devitrified sufficiently to make it opaque except for thin layers separating the cells. The cellular structure developed while the glass

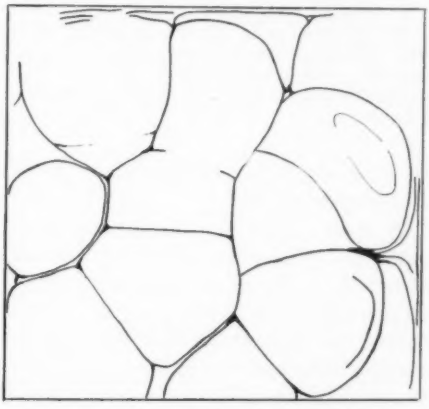


FIG. 1.—Specimen of glass having cellular structure. This specimen devitrified on cooling except for cell borders, which remained a glass. Area shown is approximately 6 inches across.

[1] Manuscript received March 10, 1948.

[2] Experimental glasses made at the Eastman Kodak Co., Rochester, N.Y.

was fluid and before devitrification occurred, but the subsequent devitrification, which did not affect the glass septa at the borders of the cells, has made the structure easily visible. The glass was poured into a square, flat-bottomed mold, flowing across the mold in a direction from bottom to top in this photograph. The ridge of glass in the central part of the bottom edge joined the lip of the crucible before the latter was removed. There is a tendency for the cells to be arranged in concentric rows about this source position.

FIG. 2.—Specimen of glass having cellular structure. This specimen partly devitrified during heat treatment subsequent to cooling. Cells are concentrically zoned. Short dimension approximately 3 inches.

A view of the top surface of three other blocks of glass exhibiting cellular structure is shown in plate 1, *B*, and figures 1 and 2. In figure 1, septa of glass delimit the cells, which devitrified during cooling. The specimen in figure 2 was entirely glass when cooled to room temperature in its mold. The devitrification, which occurred selectively within the cells, leaving the borders glassy and thereby emphasizing the cellular structure, was produced by a later heat treatment. A concentric zoning within the cells can be faintly seen. Such zoning is commonly visible within cells on close inspection but is not usually a pronounced feature. The specimen in plate 1, *B*, is all glass except for an accumulation of crystallites on the top surface. These crystallites tended to accumulate at cell intersections, thereby outlining the cells which otherwise would not be discernible in the photograph.

In plate 1, *A*, is shown the cross section and top of a specimen devitrified except for the glass border which occurs along the bottom and top as well as the sides of the cell. Commonly, the glass septa do not completely close under the cells, however, resulting in a short, columnar type of structure.

The border of the cells, as well as the top surface to the same order of thickness as the border, has a slightly different composition from the bulk of the cell as indicated by differences in refractive index. In one specimen which did not devitrify, the index of the main body of the glass and of the cell borders is, respectively, 1.65 and 1.75.

The top surface of the glass has a microscopically cellular structure. In the central part of a large cell surface (pl. 2, *A*) the tiny polygons are roughly equidimensional. Toward the borders of the large cells (pl. 2, *B*) the small polygons

PLATE 1

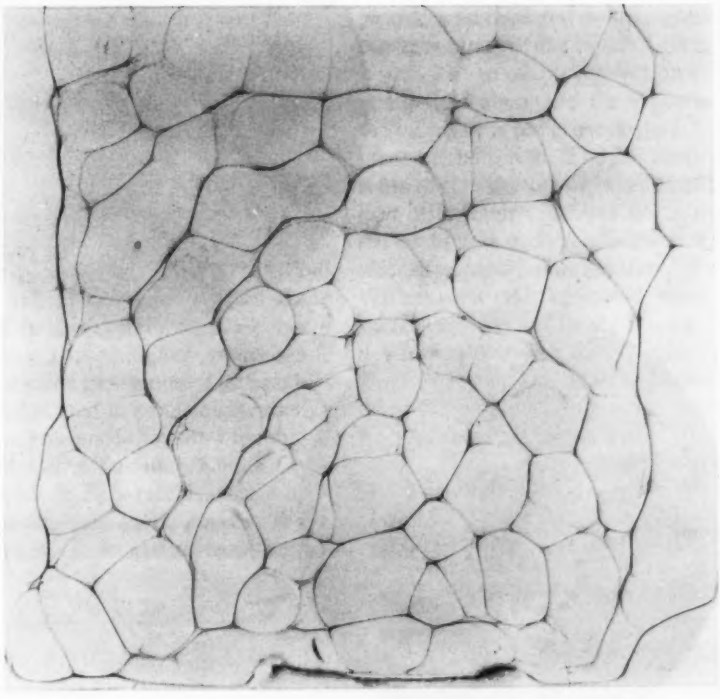
A, Top and side view of a glass specimen approximately 2 inches long, showing cross section of a cell.

B, Top surface of a specimen of glass having cellular structure. Some cells are outlined by accumulation of surface crystallites.

C, Top surface of a glass specimen exhibiting cellular structure. Specimen is 10 inches across and $\frac{3}{8}$ inch thick. Along the bottom edge of the specimen is a ridge of glass, 4 inches long, which has the position of the lip of the platinum crucible during pouring. Note tendency toward concentric arrangement of rows of cells about this source position.

A

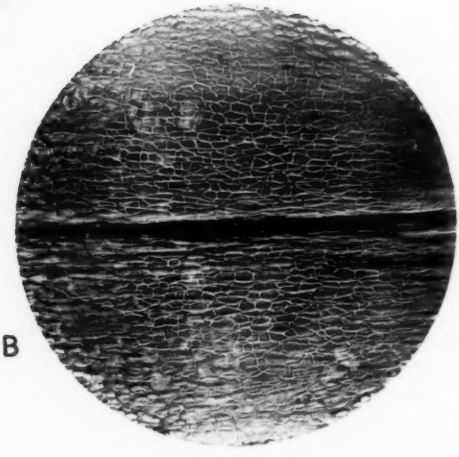
B



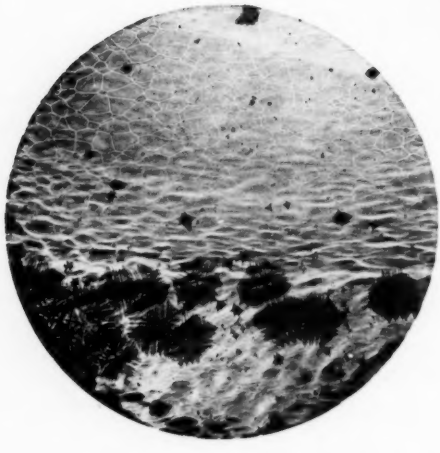
C

Cellular structures in glass

A



B



C

Cellular structures in glass

become elongated and the junctions of the large cells have a schistose appearance. Plate 2, *C*, is a photomicrograph of a part of the surface of the specimen shown in plate 1, *B*. Crystallites are present in this border zone, which grades into the central zone of regular polyhedra toward the top of the photograph.

DESCRIPTION OF THE GLASS

The glass in which the structures described above developed is a fluosilicate, composed of about equal amounts by weight of NaF, TiO_2, and SiO_2. These fluosilicate glasses are more fluid and more fuming than the usual commercial glasses owing to the large amount of fluorine substituting for oxygen in the structure. The glasses are unusual and of interest to the optical designer because of their high dispersion for a given value of n_D, but for optical use striae must be eliminated from the glass, and therefore cellular structures are obviously undesirable. Liquids in the system NaF–TiO_2–SiO_2 readily devitrify on cooling except for a limited series of compositions. The specimens shown in plate 1 and figures 1 and 2 are on the borders of the glass field in this system.

These experimental glasses were made usually in 3,000-gm. melts. The batch is melted and stirred in a platinum crucible until homogeneous, following a technique developed at the Eastman Kodak Company Research Laboratories for manufacture of the rare-earth glasses. When homogeneous and at a temperature slightly above its liquidus, the fluid glass is poured rapidly into a flat-bottomed, cast-iron mold and chilled. A slab of glass about 1 inch thick and 6–8 inches across is the usual result.

ORIGIN OF THE STRUCTURES

The cellular structures here described are a consequence of convection currents set up in the upper half or two-thirds of the glass slab during chilling. Heat is rapidly removed from the lower part of the glass layer by the cast-iron bottom of the mold. Convection currents do not tend to form in the lower part of the glass, therefore, because the temperature of the liquid increases upward. But loss of heat and volatiles from the top of the liquid produces an inverted density gradient in the upper part of the layer of glass which is sufficient to set up convection currents in the fluid glass, and these persist until the viscosity is too great to permit movement of the liquid. The convection currents divide the upper layer of the glass into cells, their diameter being dependent on factors such as thickness of layer, viscosity, and temperature gradient. Within each cell the cooled, more dense surface layer flows to the border; moves down the side to a warmer region; passes along the bottom of the cell; and then, having expanded, completes the circulation by moving upward in the central part of the cell. Such currents, if viscosity and temperature gradient remained constant until a steady state of flow developed, would produce a columnar struc-

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PLATE 2

A, Photomicrograph of top surface of glass in central part of a cell. Area shown is about 5 mm. across.

B, Photomicrograph of junction of two cells, top surface of glass. The dark band dividing area into about equal parts is glass border of cells. Scale same as in *A*.

C, Photomicrograph of a portion of top surface of specimen in plate 1, *B*, showing accumulation of crystallites along border of cells. Area shown in approximately 1½ mm. across.

ture composed of vertical, six-sided prisms. But in these glasses viscosity and temperature gradient change rapidly, the liquid mass has a horizontal and turbulent flow for the first few seconds as it fills the mold, and the convection flow is halted shortly after it begins by the rapid increase in viscosity of the glass. Consequently, well-developed columnar structure rarely appears. Globular shapes with flat tops and frequently rather indistinct bottoms, and forms intermediate between this and columns, are usual.

Convection cells are visible in the hot liquid almost immediately on its being poured and sometimes can be seen in the liquid as it is flowing across the mold. The cell outlines appear as red lines of a darker color than the central part of the cells. During the first few seconds after the mold is filled the cell borders shift slightly in position as thermal gradient and viscosity change, but the final pattern of cells is essentially the same as that which first appears, and commonly this pattern is affected by the direction and speed of movement of the liquid across the mold. In plate 1, *C*, a tendency toward a concentric arrangement of rows of cells about the point of issuance of the liquid into the mold can be seen.

Cellular structures are preserved in these fluosilicate glasses because of the properties of differentiated liquids and rarely by accumulation of crystals. The borders of the cells are a differentiate of the glass both chemically and physically. The top layer, which by flowage becomes the border, loses volatiles and cools as it moves from the central part of a cell to the border. The loss of volatiles results in the glass having a higher refractive index. Both the loss of volatiles and the more rapid cooling make the border glass more resistant to devitrification than that in the interior of a cell. If crystallites form in the surface layer, these may be carried by the glass currents to the cell borders outlining the cells, a process which apparently occurred during cooling of the specimen shown in plate 1, *B*.

RELATION OF STRUCTURES TO THOSE IN LAVAS

A fluid layer of basaltic lava flowing over a surface of low relief and cooled principally by heat loss from its upper surface should contain convection currents. Inasmuch as the rock over which the flow spreads is a poor conductor and might even be a previous warm flow, heat removal from the base would be relatively slow in contrast to the rapid removal of heat from the base of a fluosilicate glass layer by cast iron. Convection flow therefore would be expected to affect nearly the entire thickness of the lava layer, causing a chilled surface layer to move downward toward the bottom along a curved path. Horizontal movement of the lava coupled with convection flow might produce ellipsoidal structures visible because of chilled borders. These structures could be preserved if the cooling of the lava, as by contact with water, were sufficiently rapid. Were the lava to come to rest long enough for an approach to a steady state of convection flow to appear, resulting columnar structures might be visible in the solidified rock.

If the lava were extruded over a wet surface, absorption of an appreciable amount of water by the silicate liquid might occur, as described by Sosman for the case of blast-furnace slags (Sosman, 1947, p. 287). The higher water content of the lower part of the layer of lava would lower both its density and its viscosity, and this could be an additional factor in producing convection flow in lava streams.

Experiments with fluosilicate glasses

are on such a small scale as compared with lava flows that comparisons may not be justified. Some field observations, however, are suggestive that ellipsoidal structures in lavas may result from a combination of convection and lateral flow. In describing the great outpouring of lava at Mauna Loa in 1859, Green states (1887, p. 163):

> When it first broke out the lava formed a fountain of white-hot highly liquid lava, which played steadily for many days, gradually lowering, however, till finally it simply ran over, flowing down the mountain under its own cooled crust without any sign of steam, vapor or gases proceeding from it from its source to the sea at Wainanalii, a distance of about forty miles. Here we watched this molten lava pouring into the sea for several hours. It ran over a low shelf about ten feet high, and extended perhaps 500 or 600 feet wide, and fell into the sea where it was about 20 or 30 feet deep. It came from under the crust in great red-hot flattened spheroidal masses, having something the appearance of masses of moderately thick porridge as it is poured from a saucepan. The spheroidal masses, however, being perhaps 10 feet to 15 feet wide, and 4 to 6 feet deep. There was no steam, vapor or gas whatever to be seen coming from this lava till it went underwater. Indeed the first contact of the red-hot spheroids did not seem to produce a particle of steam, and it was only when each had gone under water and become partially cooled off, that a puff of steam rose above the surface.[3]

Green's "great red-hot flattened spheroidal masses" of which the lava layer was composed are considered by the writer to be convection cells, similar but on a larger scale to those in a fluosilicate liquid as it moves across the mold. Although the spheroidal masses in the lava are much larger, the ratio of width to depth is about the same as is usual for cells in the fluosilicate glass. It is considered probable by the writer that on being immersed in the water the spheroidal masses maintained their identity and built up a deposit of pillow lava.

In the subglacial extrusions of basalt in Iceland, globular basalt similar to pillow lavas of other areas is common (Noe-Nygaard, 1940). In describing one occurrence Noe-Nygaard states (1940, p. 57): "Following the globular basalt in a southerly direction we find that it passes smoothly into a basalt without globular structure, but with pronounced columnar structure (irregularly oriented columns)." The smooth gradation of globular into columnar structure suggests that the origin of both was associated with convection flow, a more nearly steady state of flow having been reached where a columnar structure developed.

ACKNOWLEDGMENTS.—The writer wishes to thank Mr. P. F. DePaolis of the Eastman Kodak Company for his co-operation in supplying most of the glass specimens used in this study. He is indebted also to Dr. H. E. Merwin, Dr. R. B. Sosman, and Professor J. T. Stark for their criticisms of the manuscript.

[3] Some additional information about this lava flow is given in Hitchcock (1911), p. 103. Hitchcock states: "Mr. W. L. Green observed the entrance of the lava into the sea, both in January and several months later: 'The red hot lava was quietly tumbling into the sea over a low ledge, perhaps six or eight feet high, and five hundred to six hundred feet long. The lava did not seem to be quite so liquid, or of such a bright color. . . . It ran more like porridge in great flattened spheroids, which were sometimes partially united together, and sometimes almost separate. . . . There was no steam to be seen escaping from the lava, and it was not until after each spheroidal mass had disappeared for a second or two under water that puffs of steam came to the surface. . . .'

"Mr. Green remarked that this tendency to form spheroids in the molten state might have some connection with the origin of basaltic columns, as well as to weathered spheroidal masses seen in ancient lava streams. . . . He allows that there was nothing like compression: the great flattened spheroids rolled quietly over into the sea, causing a slight commotion in the water."

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GEOLOGICAL NOTES

NATURALLY BRIQUETTED COAL FROM A BED IN WESTERN PENNSYLVANIA[1]

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In the spring of 1945, while I was associated with the United States Bureau of Mines, I received from Dr. Elmer Kaiser, of Bituminous Coal Research, Inc., a very peculiar specimen of coal that was spheroidal in form and about the size of a golf ball. A section across this spheroid showed that granular and pulverized coal had been consolidated around a single larger fragment of coal that served as a nucleus.

The illustrations show the cut surfaces of halves of this nodule, prepared in slightly different ways and photographed, using slightly different modes of illumination. The half shown in plate 1, *A*, has been polished dry, and the surface presents a minimum of relief. Some concentric arrangement of granules is evident, and the nucleus shows normal banding—a feature which is not very evident, however, from this photograph. Two flecks of disseminated pyrite that indicate the plane of banding are more distinctly visible. The specimen was photographed with illumination from a relatively low angle, under which condition polished coal surfaces appear black.

The half that is illustrated in plate 1, *B*, has been gently polished wet on selvyt cloth with optical-grade cerium oxide and shows a central cavity where the nuclear coal broke away. Care in polishing did not prevent development of very high surface relief, and it is clear that the nodule would disintegrate under continued wet conditions. Illumination for this photograph was from a relatively high angle, and the nodule was tilted slightly so that polished coal fragments in the peripheral zone reflected light directly into the camera lens and thus appear white in this picture.

Observed under similar conditions with the Greenough type microscope, the larger fragments of coal appear normally banded, perhaps to a considerable extent microbanded, with dominantly bright luster. A fragment of the peripheral shell was prepared in a thin section at the Bureau of Mines laboratory by Mr. H. J. O'Donnell. The very fragile character of the moistened material occasioned some losses, but an adequate section was obtained for observation. When observed at higher magnification under the biological type microscope by transmitted light, the coal appears mostly vitrinized, much of it of a nature comparable to anthraxylon. It is, however, pulverized to a remarkable degree. Aside from this, it is comparable to bright, high-volatile bituminous coal as in the Lower Kittanning and most of the other coal beds of western Pennsylvania.

Dr. Kaiser transmitted one specimen to me originally, and three additional specimens were subsequently obtained. One of these has been kept intact; the other two were sliced, and they also show an angular coal fragment in the center and a "shell" of pulverized coal with slight concentric layering similar to the specimen illustrated. All have the same type of evenly rounded, slightly roughened dull surface on the out-

[1] Text of an informal communication presented before the Geological Society of Washington, March 24, 1948. Published by permission of the Director, U.S. Geological Survey. Manuscript received May 3, 1948.

side, with no external cracks or fissures. The only indication of cracks in the shell is seen on the cut surfaces opposite and radiating from the angular corners of the nuclear piece of coal in the center (pl. 1, *A*, and at the back of the central depression of pl. 1, *B*). The nodules are sufficiently coherent that the shell has a tendency to yield shallow, more or less concentric spalls rather than to break across or around the nucleus.

A portion of the pulverized coal shell from one specimen was submitted to Mr. H. M. Cooper, of the Bureau of Mines Coal Analysis Section, for ash and specific-gravity determinations. The following values were obtained: 17.87 per cent ash, as received; 1.474 apparent specific gravity. The ash appears to be chiefly in the form of finely dispersed clay distributed among the pulverized fragments.

The indirect knowledge of the occurrence in the first place has, unfortunately, prevented a close firsthand appraisal of all the circumstances that might have bearing on the origin of these unusual aggregations. It seems that Dr. Kaiser obtained the specimen he sent me from Mr. Raymond, of the New York Central Railroad, who had received it from inspectors of the railroad, Mr. McHugh and Mr. Cavanaugh, who had, in turn, observed them at the tipple and made some inquiry about them from the mine superintendent, Mr. George H. Henderson. Mr. Henderson had previously noticed the nodules incidentally when they came to the mine tipple, had inquired about their point of origin, and later saw a considerable quantity of them at the pit but had not taken a particular interest in them at that time. When my inquiry finally reached him, this particular pit had been exhausted of accessible coal and was closed. A watch for other occurrences of similar nodules has been maintained since then, but no others have been found. The three nodules sent following my inquiry were discovered by Mr. Henderson at the tipple. Presumably all were from the one original occurrence.

The following details regarding the occurrence are based on a recent interview with Mr. Henderson and an inspection of the locality. The coal is now covered by a considerable amount of talus and could not be directly observed in this old strip pit.

The coal bed in question is the Lower Kittanning. It is about 24 inches thick at this point and overlain normally by some 30 feet of dark-gray shale. The shale is fairly massive-appearing and tough when fresh, though lenticular ironstone concretions are present, but it soon disintegrates on weathering and bleaches to a lighter-gray or buff color. One bony parting is present in the coal, varying from about ½ to 1 inch in thickness and located about 8–10 inches from the top of the bed. This parting was seen at another mine, where it was said to be similar. The bony parting has dull luster, is tough, and varies in general megascopic appearance from a moderately high-ash durain to the tough, shaly, carbonaceous rock characteristically known as "bone." The nodules in question are said to occur *in the coal* for 3 or 4 inches below this bony parting. At the one location where they occurred, the nodules are reported as sticking out of one side of horizontal fracture surfaces of the coal from this layer, leaving a counterpart hemispherical depression on the opposite surface. There is no doubt that the majority of the coal in the bed is normally banded, but a question must remain as to the precise character of the coal inclosing the nodules because no specimen was saved, and at the point where the nodules were found the coal might be different from that normally in this posi-

PLATE 1

A, Median section of spheroidal natural briquette, polished dry; angular central coal fragment shows obscure banding (horizontally oriented on the page). Coal fragments appear black.

B, The opposite half of briquette shown in *A*, polished wet, showing considerable relief owing to loss of fine matrix and the nuclear fragment. Larger upstanding polished surfaces of coal fragments appear white in this photograph. Photographs by the author.

Median sections of naturally briquetted coal

tion elsewhere. A normal underclay is said to occur below the coal bed.

The strip pit where the nodules were found is on a small eastward-facing nose of the hill crest just south of Piney Dam on Clarion River. It is located about 3 miles south and 2 miles west of Clarion, Clarion County, in the northwestern part of Pennsylvania. The pit encircles the nose at the level of the Lower Kittanning coal (elevation about 1,400 feet as judged from the 1907 edition of the Clarion quadrangle topographic sheet, reprinted in 1943) to the extent of two or three normal-width "cuts" taken with the electric shovel. The operation was closed when overburden increased to more than 40–50 feet, the present economic limit for the thickness of coal available. The nodules were observed close to the easternmost extension of this strip pit.

The formation of such spheroidal aggregations of pulverized coal is still most puzzling to the writer. The coal composing them was evidently physically similar to bituminous rank coal when they were formed, as shown by the angular fracture edges of the nuclear piece as well as by the angular, comminuted pieces composing the shell. The spheroids are remarkably symmetrical and show no indication of any compression. Not even the internal structure appears to yield any clue in this direction. They are about as hard as lumps of bright coal of the same size would be and less fragile because of the lack of cleating. The ash content of the nodules is considerably higher than average for this bed, and it seems likely that their coherence is partially a result of clay functioning as a "binder" for the pulverized coal fragments. Evidence for this is the tendency of the aggregation to disintegrate under wet grinding and polishing.

These features have implications as to mode of origin, but the suggestions are not easy to reconcile with the well-established usual concepts of coal formation.

It would seem necessary to assume that the coal fragments in the nodules are probably foreign to the Lower Kittanning bed since they must have been physically coalified when the coal they were embedded in was only in the peat stage. It is evident the Lower Kittanning material was easily deformed when the nodules were introduced to this coal bed.

It is obvious that the nodules are not truly concretionary—that chemical processes of solution and reprecipitation, such as are characteristic of mineral concretions, have nothing to do with them.

The aggregation of coalified fragments into symmetrical spheroids could occur only under special circumstances involving rotation in *all* planes around the central nucleus; rotation in even approximate alignment along any single axis would have produced initial axial elongation, a feature that is clearly lacking. One may obtain the type of rotation inferred for the coal spheroids in very special instances of accretionary growth in mud balls or in the organic aggregations Kindle (1934) refers to as "lake balls."[2]

A question must remain as to how the finely pulverized coal of the "shell" could ever have formed under natural conditions. Evidence of the relatively early physical incoalation of beds in Carboniferous times is found in the fairly common occurrence of water-rounded coal pebbles incorporated in the conglomeratic basal zone of channel sandstones in the Pennsylvanian. Such pebbles, like the larger fragments in the nodules, show definite indications of cleating. But the particles and fragments of the accretionary shell of the spheroids described here have no appearance of forming by any processes normal to erosion; they all are sharp and angular and show no evidence of ordinary size segregation or sorting beyond the fact that pieces larger than about 1 mm. were not incorporated in the shell. Smaller pieces of all visible sizes are included, so that whatever size selection existed, apparently acted in reverse of that normally considered affecting size classification. This is, of course, consistent with an accretionary mode of ag-

[2] The coal balls of paleobotanical studies are never accretionary as Kindle suggests; their mineral matrix is truly concretionary.

gregation. Fault gouge material could include similarly unsized angular fragments, but a sufficient supply of coal crushed in this manner and exposed so that numerous accretionary spheroids could be formed at the time of Lower Kittanning coal deposition is difficult to imagine. The writer knows of no collateral evidence that would suggest this remote possibility.

The lack of secondary compressional distortion of the spheroids by compaction of the Lower Kittanning coal matrix is also hard to understand, yet it must be accepted if the place of discovery is accurately reported, and the writer sees no basis for questioning it. It is possible that some types of attrital coal may have a relatively rapid dehydration-compaction cycle in diagenesis, which is not well understood. The matrix surrounding the spheroids was not examined, and it is possible that it, too, consisted of a pocket of consolidated pulverized coal whose character was not particularly evident on casual inspection. If the immediate matrix consisted of "prelithified" coal fragments, the lack of secondary compression effects in the spheroids would be easier to understand. Under the moderate pressures implied by the present rank of the Lower Kittanning coal in this area, a microbreccia of previously consolidated coal might show imperceptible diagenetic compression like a lens of sandstone.

Enough has been said to give some idea of the highly anomalous character of these spheroids. As the title of this note suggests, the writer regards them as examples of naturally "briquetted" coal because of their obvious but superficial analogy with ordinary commercial briquettes. No similar occurrence is known to be reported.

It is obvious that the natural briquettes have no similarity with the "niggerhead" nodules or coal "pebbles" or "apples," chiefly known now in America from the Walsenburg district in Colorado, though also reported by others (Stutzer, 1940) or observed by the writer from the anthracite and southwestern districts of Pennsylvania, near Red Lodge in Montana, in Alaska, Peru, Poland, Hungary, France, northern Italy, India, the Transvaal, and Australia. These arise from an unusual type of spheroidal spalling consequent to normal rectangular cleating, and close observation shows that there is no derangement of the coal in the bed. Coal balls are essentially a type of true mineral concretion in coal beds and, likewise, have no bearing on or relation to the spheroidal "briquettes" described here. Sometimes large examples of vertical conchoidal cleating (eye-coal, "augen"; Stutzer, 1940, pp. 249–253) in coal of homogeneous lithology have been mistaken for spheroids of one kind or another broken in half, but these features must be related to a very different type of phenomenon. The manner of origin of the natural briquettes is another of the many unsolved mysteries about coal.

The specimens described in the foregoing communication have been deposited for reference in the mineral collections of the United States National Museum under catalog no. 108467.

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STYLOLITES IN PRE-CAMBRIAN QUARTZITE[1]

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INTRODUCTION

The stylolites here discussed came to the writer's attention during the petrographic study of a suite of gneissic rocks from the Ace Lake area, some 8 miles north of Goldfields, Saskatchewan. Alcock (1936) included these rocks with granite and gneisses in one mappable unit, which he considered to be of Archean age, younger than the Tazin group and older than the Beaverlodge series of early Proterozoic age. Recent work by A. M. Christie,[2] of the Geological Survey of Canada, has cast some doubt on the validity of separating the Tazin group and the Beaverlodge series. The metamorphic rocks in the Ace Lake area may therefore be referable to either the Tazin group or the Beaverlodge series.

ORIGIN OF STYLOLITES

The question of whether stylolites are of primary or secondary origin has been widely discussed. There is a difference of opinion even with reference to the same occurrence of stylolite seams in the Pottsville quartzite of Lookout Mountain, Alabama. Shaub (1947, p. 116) believes them to be "entirely due to the usual processes of deposition of cross-bedded sands together with the adjustments occurring during compaction up to the time of the consolidation of the sandstone." On the other hand, Stockdale (1945, p. 135) states:

> Instead of being developed as primary structures along normal planes of sedimentation at or near the time of deposition of the original sediment (sand), the stylolite-seams came into being as secondary features subsequent to the original deposition and compaction of the sediments. They were developed along fracture-partings which originated at a time not only later than the original consolidation of the sediments into sandstone but even later than the metamorphism into the quartzite. Thus there is revealed another finding to be added to the already existing preponderance of evidence in support of the belief that stylolites are of secondary origin as held by the solution theory.

According to Stockdale (1943, p. 3):

> The *solution theory* contends that stylolites result from differential chemical solution in hardened rock, under some pressure, on the two sides of a parting of some sort (such as a bedding plane, lamination plane, suture, or crevice), the individual portions of the one side fitting into the dissolved out parts of the opposite, the interfitting taking place slowly and gradually as solution continues.

In referring to stylolites in the Pottsville sandstone of Pennsylvanian age and the Medina sandstone of Silurian age, Price (1934, p. 188) expressed the view that they were due to solution of material along parting surfaces and that pressure was not a factor; for he states: "In the present examples differential solution alone can account for their origin." In contrast to this view, the hypothesis of a primary origin is advocated by Shaub (1939, p. 47), who states: "The occurrence of stylolites in sandstone and quartzite, as well as in the carbonate rocks, is readily accounted for by the contraction-pressure theory, which also explains the wide variation in form, structure, markings and other features of stylolites."

The purport of this paper is not to suggest that *all* stylolites are of secondary origin but to demonstrate that in this instance the origin could not have been primary.

DESCRIPTION OF THE PRE-CAMBRIAN QUARTZITE

The rock is a fine-grained, dark-gray quartzite, with a network of minute, quartz-filled fractures. As can be seen in plate 1,

[1] Manuscript received May 3, 1948.

[2] Personal communication.

the stylolite is more or less parallel with the foliation, which, in transmitted light, is indicated by wavy stringers of specularite and, under crossed nicols, by the elongation of the quartz grains. The grains of quartz vary in length from 0.03 to 0.1 mm. and have sutured boundaries. The elongation of the quartz grains and the sutured boundaries indicate that the rock has been recrystallized under stress. The stringers and surfaces of the stylolites are of minute specks and clusters of specks of specularite, bluish-gray by reflected light.

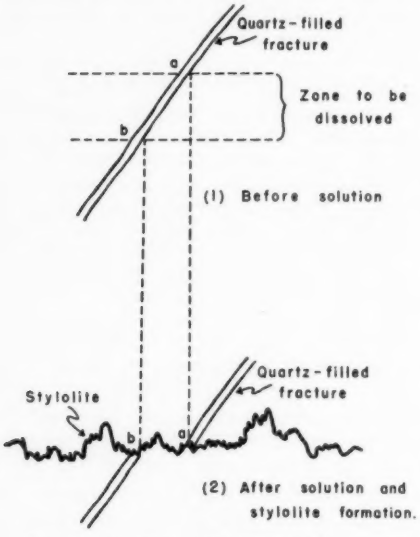


FIG. 1.—Apparent displacement of a quartz-filled fracture by a stylolite, due to solution along the cross-cutting stylolite.

RELATIONSHIP OF THE STYLOLITES TO THE QUARTZITE

An examination of the thin section illustrated by plate 1 shows that the stylolites must have developed after the recrystallization of the rock. The following points indicate the age relationship of the stylolites to the quartzite and specularite stringers.

1. The quartzite has been formed by recrystallization under stress, as indicated by the sutured quartz grains elongated parallel to the foliation. If the stylolites were of primary origin, they would have been destroyed.

2. All the quartz-filled fractures cut the specularite stringers. Furthermore, the fracture illustrated in plate 1 is a minute fault, as indicated by the displacement of the band of coarser quartz beneath the stylolite.

3. The stylolite shown in plate 1 cuts the quartz-filled fracture and must have originated after the period of fracturing.

4. The stylolites were not all formed at the same time, as several of the quartz-filled fractures cut stylolites, although they are themselves cut by other stylolites.

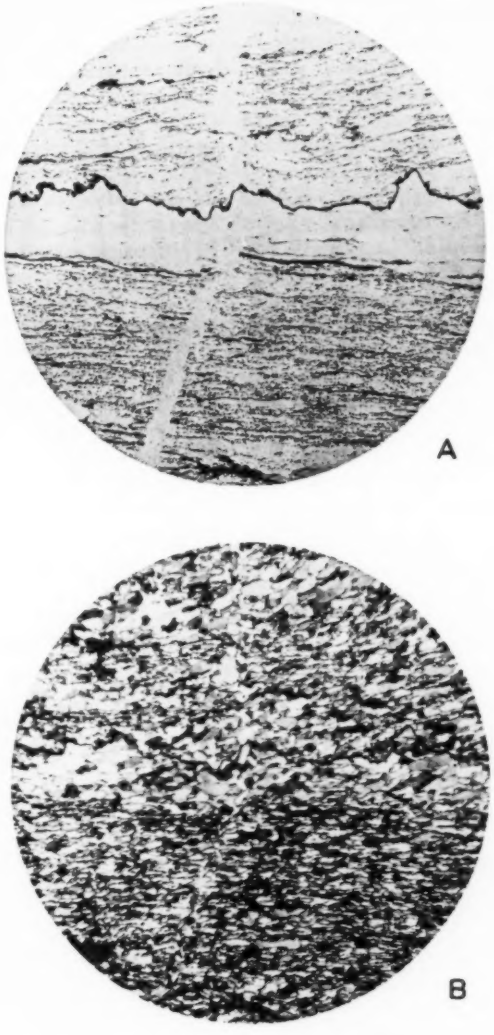
5. Where stylolites obliquely cut quartz-filled fractures, there is apparent displacement of the fractures. This apparent displacement is not considered due to movement but to the effect of solution along the cross-cutting stylolites (fig. 1).

An examination of plate 1 shows that the stylolite forms one boundary of an area of clear quartz and that other irregular lenses of clear quartz are parallel to the foliation. Plate 1, *B*, shows that the quartz grains in these clear areas are coarser than are those associated with the specularite stringers. In the adjacent rocks specularite has been introduced in abundance, and it is inferred that the specularite stringers have also been introduced and do not represent the iron content of the original sediment. Unless the finer-grained quartz offered better channels for the infiltration of iron-bearing solutions,

PLATE 1

A, Thin section of quartzite, viewed with transmitted light. The dark stringers are of specularite. Note that the quartz-filled fracture cuts the specularite stringers and is itself cut by the stylolite.

B, Same view as *A*, between crossed nicols. Note that the irregular lenses of clear quartz and the area of clear quartz adjacent to the stylolite are coarser grained.



Stylolites in pre-Cambrian quartzite

it must be inferred that the areas of clear quartz are of later development than the specularite. If so, the quartz may have been introduced or may have been locally recrystallized. Petrographic examination of adjacent rocks shows that similar quartz lenses and stringers have been introduced, and the same sequence is inferred here. As is shown by plate 1, the quartz-filled fracture cuts these areas of clear quartz.

It is inferred that the stylolites have developed by solution of the rock along partings, accompanied by the concentration of residual specularite along the surfaces of the stylolites.

CONCLUSIONS

The stylolites here described are of secondary origin and were formed after the recrystallization of the quartzite. It is demonstrated that the sequence of events in the rock's history has been as follows: First, there has been recrystallization of the original rock to a quartzite, the recrystallization having taken place under conditions of stress, as indicated by the parallel orientation of the sutured quartz grains. Second, fracturing of the rock has occurred transverse to its foliation, quartz having been introduced into the fractures. Third, there has taken place the development of those stylolites which cut the quartz-filled fractures.

In conclusion, the writer wishes to state that, while the mode of origin of the stylolites here discussed is in doubt and can only be inferred, the time of origin is unquestionably later than the period of recrystallization of the rock.

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RECENT SHORELINE CHANGES AT SHIRLEY GUT, BOSTON HARBOR[1]

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INTRODUCTION

Prior to 1936, Deer Island in Boston Harbor was separated from the mainland by Shirley Gut, a strip of water with unusually strong hydraulic currents (fig. 1). This gut was filled in by the growth of spits from Deer Island and Point Shirley.

Point Shirley, a part of the mainland, consisted of a small drumlin, from which a broad spit extended southeastward (LaForge, 1932, pl. 2). Deer Island was composed of four eroded drumlins joined by beaches. Until 1936, a spit at its northwest end terminated at Shirley Gut (Roorback, 1910).

COLONIAL AND RECENT HISTORY OF SHIRLEY GUT

There are records of boats sailing through Shirley Gut in early Colonial times. It was used in the Revolutionary War as the northern entrance to the harbor, and in 1776 a fort was built on Point Shirley to defend it. On May 19, 1776, a naval engagement took place in the Gut between the colonists and

[1] Manuscript received March 4, 1948. Published by permission of the Director, Geological Survey, U.S. Department of the Interior, and the Massachusetts Commission of Public Works.

the British. The colonists had two boats—the privateer "Franklin," of four guns and about thirty men, and the "Lady Washington," a schooner carrying twenty-five men. A strong force of more than two hundred British in small boats attacked the schooners. The colonists overturned many of the British boats, and the men who were plunged into the waters of the Gut were carried away from the scene of the battle by the swift currents. The British were repulsed and are said to have lost seventy men and several boats, but the colonists lost only one man. Up to about 1900 the Gut was used by boats of two or three hundred tons, some of

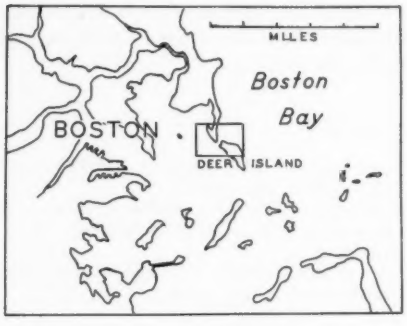

FIG. 1.—Index map of Boston Harbor, Massachusetts. Area considered in text outlined.

which carried passengers to Nahant and elsewhere. Since 1900 the Municipal House of Correction has been on Deer Island, and the Gut has served as an effective barrier against escape, for the currents are so powerful that only the strongest swimmers could reach the mainland.

CLOSING OF SHIRLEY GUT

The growth of the Point Shirley and Deer Island spits, as well as the filling-in and destruction of Shirley Gut, is shown in figures 2, 3, and 4. In 1860 the average width of Shirley Gut was 700 feet. By 1898 its width had decreased to 400 feet; in 1934 it was only 80 feet wide at its narrowest point; and in 1936 Deer Island was joined to Point Shirley by a strip of land which was 300 feet wide at mean tide and completely flooded only by exceptional tides (figs. 2 and 3). In places the Point Shirley spit grew approximately 400 feet in the period between 1860 and 1934. Before 1936 the northwestern end of Deer Island was a double-pronged spit. The bayward prong on the south side of the spit was relatively inactive between 1860 and 1934, although in places the oceanward prong grew nearly 750 feet during the same period.

While these spits were growing toward each other, the Gut was also being filled in (fig. 4). In 1847 the maximum depth of the Gut at high tide along the profile shown in figure 4 was 45 feet. This depth was due partly to scour. In 1861 it was 35 feet, and in 1934 about 11 feet. An analysis of the profiles shows that the filling did not take place uniformly, as there were both cut and fill.

CONFLICT BETWEEN HYDRAULIC AND LONGSHORE CURRENTS

During the existence of the Gut there was a continual conflict between the hydraulic currents running through it and the longshore currents which formed the spits. The former tended to keep the Gut open, whereas the latter, in general, tended to fill it. The strength of the hydraulic currents depended mainly upon the tidal range and the force and direction of the wind, and the strength of the longshore currents depended upon the force and direction of the waves. The strengths of both the hydraulic and the longshore currents varied greatly with continual changes in the direction and force of the wind and waves and with changes in the tidal range. It is not surprising, therefore, that the filling of the Gut did not proceed at an even pace. As the Gut narrowed, the currents in it became stronger, so that the tendency to fill diminished. Just before the joining of Deer Island and the mainland, however, the volume of water going through the Gut was decreased; the erosive effect of the currents was consequently diminished, and the filling proceeded rapidly.

The currents at the bottom of Shirley Gut had velocities at times in excess of 1.7

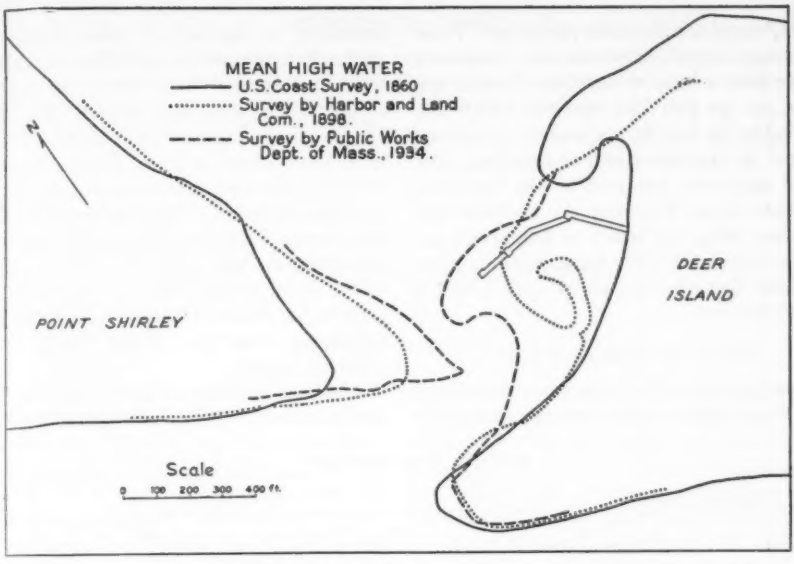

FIG. 2.—Map of Shirley Gut in 1860, 1898, and 1934

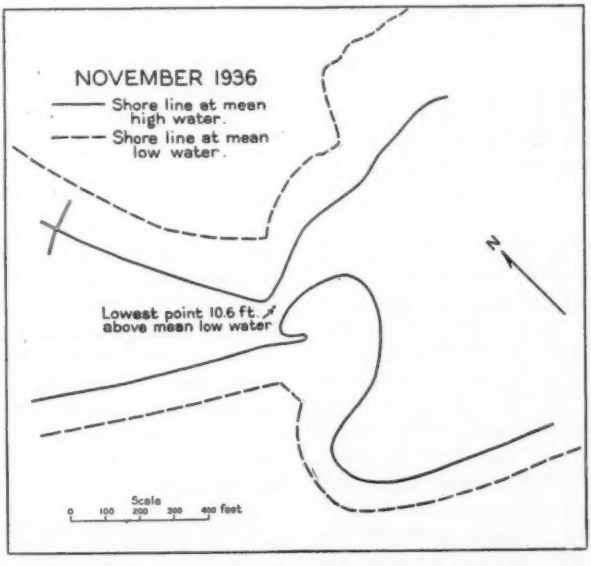
NOVEMBER 1936
Shore line at mean high water.
Shore line at mean low water.
N
Lowest point 10.6 ft. above mean low water
Scale
0 100 200 300 400 feet

FIG. 3.—Map of Shirley Gut in 1936. Map by R. L. Nichols and Louis Riseman

knots,[2] equal to 0.87 meter per second. These velocities could have moved fragments larger than a bean or hazelnut (Twenhofel, 1932, pp. 40–41). The material which was carried to the Gut by the longshore currents ranged in size from silt to boulders. The small sizes were removed by the hydraulic currents in the Gut, but the boulders and cobbles, being too heavy to be moved, accumulated in the Gut. Soundings made before the Gut closed showed that it had a gravel bottom.

GROWTH OF DEER ISLAND SPIT

The growth of both the Deer Island and the Point Shirley spits was responsible for the joining of Deer Island to the mainland. The north prong of the Deer Island spit prograded more rapidly than did the Point Shirley spit prior to the closing of the Gut. This is indicated by the following facts: (1) The data afforded by figure 2. (2) Before the closing of the Gut, the material of Point Shirley Beach systematically varied in size from place to place.[3] At Winthrop Head, which is north of Point Shirley (fig. 1), the beach was composed of coarse gravel; southward the beach material gradually decreased in size; and, still farther south and extending to the end of Point Shirley, it gradually increased in size. The coarse material at the end of Point Shirley was drifted across the Gut from Deer Island. This could have been accomplished only if the currents from Deer Island to Point Shirley were, in the main, stronger than those moving in the opposite direction. This fact suggests that the growth of the Deer Island spit was more important in closing the Gut than was that of the Point Shirley spit. (3) Immediately prior to the closure, the Deer Island spit was advancing over the Point Shirley spit (Nichols, 1938).

The closure of Shirley Gut, as is indicated by figure 2 and an analysis of the longshore currents, resulted from the movement of material along the ocean side of the two spits. After the closure was completed, a small spit grew southeastward from the bay side of the former Point Shirley spit (center, fig. 3). If man had not interfered with the normal shoreline development, this small spit in time would have reached the former Deer Island spit, and a small pond would have been formed.

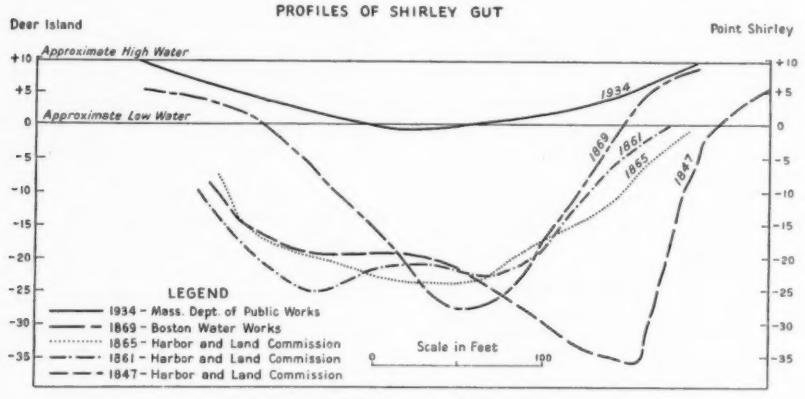

FIG. 4.—Transverse profiles of Shirley Gut

ACKNOWLEDGMENTS.—Thanks are due to Dr. L. W. Currier, of the U.S. Geological Survey, for help in the preparation of the manuscript, and to Messrs Theodore Botinelly and Louis Riseman, both of Tufts College, for assistance in the mapping.

[2] L. P. Disney, personal communication, 1942.

[3] A. C. Lane, personal communication, 1936.

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ROCKS OF THE MID-ATLANTIC RIDGE[1]

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A remarkable achievement by the Atlantis expedition (1947) of the Woods Hole Oceanographic Institution, under the leadership of Professor Maurice Ewing, was the recovery of several hundred pounds of boulders from depths approaching 2,500 fathoms over the Mid-Atlantic Ridge. Some of these boulders are of limestone and will be described elsewhere, but a large proportion consists of eruptive rocks referable to the following groups: (1) holocrystalline gabbroic rocks, (2) basalts (pillow lavas) with and without olivine, and (3) serpentines. Table 1 gives the latitude and longitude of each station where these boulders were collected, together with the depth and the kind of rock.

PETROGRAPHY

GROUP 1—HOLOCRYSTALLINE GABBROIC ROCKS

Station 5, no. 1.—This is a fresh olivine gabbro of grain size ½–1 cm. It contains hypidiomorphic to rounded grains of olivine, sometimes with narrow rims of talc (?) and magnetite. The olivines are in many cases enclosed in larger individuals of clinopyroxene (augite with polysynthetic twinning). The plagioclase is a medium labradorite having an imperfect ophitic relation toward augite.

Station 6, no. 3.—This rock may be described as a crushed anorthositic gabbro. Corroded plates and prisms of diallagic pyroxene, some as much as 2 cm. long, are surrounded by collars of granulated material of the same appearance. These aggregates lie in a fine, sugar-grained groundmass of plagioclase, within which the pyroxene forms dark streaks and eyes. The larger pyroxene fragments have a micaceous cleavage, and the cleavage cracks are strongly curved. In consequence of this curvature, with the accompaniment of wavy extinction and minute polysynthetic twinning, it was found impossible to make any reliable measurements of optical orientation or axial angle. The same difficulty recurred in the case of the plagioclase grains; in many of these the polysynthetic twinning is faint or almost absent, and in the few grains that seem to show distinct lamellae, it appears, when the grain is examined on the universal stage, that each lamella is made up of a great number of thinner lamellae of which no measurements could be made. All that one can say of this plagioclase is that the mean refractive index is well above that of Canada balsam. The grains of the granulated pyroxene are mostly between $\frac{1}{100}$ and $\frac{1}{1000}$ mm. They fit closely together, and films of brown biotite lie along the junctions. The larger plagioclase grains are of the same dimensions, but where crushing has been most intense the smaller grains have been so closely compacted that the boundaries are not sharply discernible.

Station 20, no. 6.—This specimen is a coarse and remarkably tough diabase, in which plagioclase laths 1–3 mm. long are enclosed in skeleton crystals of augite several times that size. Little, rounded grains of

[1] Manuscript received July 19, 1948.

olivine, transforming externally into iddingsite, are also present. This rock is a perfectly normal olivine diabase.

GROUP 2—BASALTS WITH AND WITHOUT OLIVINE

Station 7, no. 1.—The specimen is a fine-grained gray rock with a few little insets of plagioclase and olivine. One end of the specimen shows a distinct curvature and bears a skin of shiny black glass. Perpendicular to this skin, the rock shows vestiges of a radiating columnar structure, indicating that the specimen is part of a lava pillow. A thin section was cut about 6 inches beneath the glassy skin. Under the microscope it showed about 5 per cent of olivine insets, measuring 0.25 mm. or less and remarkable for their perfect freshness. A network of thin plagioclase laths ranging in length from 1.5 mm. to the limit of visibility, lies in an imperfectly crystallized groundmass consisting of augite granules, feldspar microlites, and semiopaque matter. There is no glass. The extinction of the plagioclase laths indicates a rather calcic labradorite.

Station 7, no. 3.—A thin section, cut about 3 inches beneath the glassy crust of this specimen, is generally similar to no. 1 but less completely crystallized. There are many little idiomorphic insets of olivine, holding oriented inclusions of the groundmass. The latter consists of radial groups, brushes, and sheaves of very thin plagioclase laths, separated by, and to some extent including, some semiopaque dark glass or near-glass.

Station 7, no. 5.—A thin section of the glassy crust of this sample shows a perfectly isotropic, clear yellow-brown glass containing little insets of olivine and plagioclase, but no augite. Each of the plagioclase laths is surrounded by a mantle of darker-colored glass, which, under high magnification, seems to have a fibrous structure. It was not possible, however, to determine the nature of these mantles with certainty. There are also many minute or incipient crystals in the glass, each surrounded by a dark mantle. The olivine crystals show no such mantle. Fuller (1932, p. 107) has described similar dark mantles about crystals of plagioclase and augite in a basaltic glass (sideromelane) from the Columbia River basalts. He considers the mantles to represent "a transitional step in the development of an opaque ground composed of dustlike particles and thin needles of magnetite." It is self-evident that the crystallization of feldspar from an iron-containing glass must enrich the surrounding glass with iron, while the crystallization of olivine uses up iron and therefore generates no dark mantle.

Station 7, no. 7.—This rock is identical with no. 1.

Station 7, nos. 4 and 6.—These specimens are so similar to those described above that they were not studied under the microscope.

Station 8, no. 1.—This fragment is brown and much altered. It is again an olivine basalt, but the olivine is largely altered to an iddingsitic material. The groundmass contains spongy iron hydroxide, and vesicles

TABLE 1

Station	Latitude	Longitude	Depth (Fathoms)	Rocks
5.....	30°00′	42°10′	2,100–2,500	Single specimen of olivine gabbro
6.....	30°06′	42°08′	800	Crushed anorthositic gabbro; much serpentine; no basalt
7.....	30°01′	45°01′	2,340	Basalt only
8.....	31°49′	42°25′	1,700–2,100	One fragment of weathered basalt
10.....	31°55′	40°26′	1,450–1,500	One sample of basalt
20.....	34°04′	42°16′	2,250	Much basalt; much serpentine; one coarse diabase
21.....	30°08′	43°37′	2,300	Much serpentine; no basalt

are lined with bright-green chlorite or filled with fibrous zeolites.

Station 20, no. 2.—In this specimen, insets of glassy plagioclase, up to ½ cm. in diameter, and a few small augites lie in a dark-gray, fine-grained base with many minute vesicles. On the universal stage the augites show an axial angle of 52–54 (positive). The indicated composition of two albite-carlsbad twins of plagioclase was Ab_{65} and Ab_{70}, respectively. Olivine is also present among the insets. The groundmass consists of little plagioclase laths and some olivine grains, the interstices filled with a semitransparent, cryptocrystalline matrix. All the insets are perfectly fresh.

Station 20, no. 3.—This basalt seems to be free from olivine, not even represented by serpentine or iddingsite. Abundant thin laths of plagioclase, containing inclusions of the groundmass, form radiating groups and brushes in a rather indistinct ground of smaller plagioclases and little prisms and grains of augite, with small amounts of calcite and chlorite. There is no true glass.

Station 20, no. 4.—A very fine-grained, dark-gray rock without visible insets of any kind. Under the microscope a few platelets of plagioclase may be seen, but the bulk of the rock is spherulitic. Neither olivine nor augite has crystallized.

Station 20, no. 7.—A rather unfresh basalt with semiophitic texture. No olivine seems to be present, although the matrix contains greenish decomposition products, in addition to augite and plagioclase.

GROUP 3—SERPENTINES

Station 6, no. 1.—Antigoritic serpentine has almost completely replaced original olivine, of which only a few scraps survive. Large plates of bastite presumably represent an original pyroxene. The rock is cut by veinlets of chrysotile. Iron oxides, talc, and carbonates are other secondary products.

Station 6, no. 2.—This specimen is like no. 1, but the olivine is completely replaced.

Station 20, nos. 1 and 5.—In addition to varieties of serpentine, these rocks contain tremolite and a few grains of brown spinel (chromite?).

Station 21, no. 1.—This specimen is a mass of tremolite asbestos.

Station 21, no. 2.—This rock is another bastite serpentine with some residual olivine.

DISCUSSION

Our knowledge of the composition of the Mid-Atlantic Ridge has been derived hitherto from the islands and island groups which are scattered at long intervals along its course, namely, Gough Island, Tristan d'Acunha, St. Helena, Ascension, St. Paul's Rocks, and the Azores. On every one of these islands the dominant rock is basalt, generally olivine-bearing but sometimes free of this mineral. Other rocks which have been recorded are as follows:

Gough Island.—Essexite, trachyte, sodalite-trachyte, phonolite (Campbell, 1914; Smith, 1930; Barth, 1942).

Tristan d'Acunha.—Pyroxenite, trachyte, phonolite, single boulder of muscovite-biotite gneiss or granite (Schwarz, 1905; Smith, 1930).

St. Helena.—Trachyte, phonolite (Daly, 1927; Smith, 1930).

Ascension.—Trachyte, rhyolite, obsidian, boulders of granite, diabase, gabbro, peridotite (Darwin, 1876; Renard, 1889; Reinisch, 1912; Daly, 1925).

St. Paul's Rocks.—Mylonitized dunite (with hornblendic and enstatitic facies) (Renard, 1879, 1882; Washington, 1930; Tilley, 1947).

Azores.—Trachyte, essexite (John, 1896; Reinisch, 1912; Friedlaender-Esenwein, 1929).

The Atlantis collection confirms the predominance of basalt and makes at least two notable additions to the record, namely, an abundance of serpentine and a mylonitized anorthositic gabbro. The latter, together with the dunite-mylonite of St. Paul's Rocks, provides evidence of strong shearing stresses during or after the formation of the Ridge. The serpentines show advanced hydration and other degenerative changes, whereas the olivine-basalts are just as fresh

as random samples of any recent terrestrial basalt and contain unaltered olivine. Thin veinlets of serpentine cut the St. Paul dunite, but the very slight degree of serpentinization in this rock and in the olivine-basalts contrasts strongly with the almost complete hydration exhibited by the serpentines. This seems to justify a suggestion that the serpentine may be appreciably older than the basalts.

Professor R. A. Daly has shown by comparison of chemical analyses that the basalts of Ascension Island differ in no essential respect from the average basalt of the continents. He concludes that the similarity of these averages illustrates "the relative uniformity of common basalt throughout the world" (1925, p. 73). The basalts of the Atlantis collection support that conclusion. They show no mineralogical or textural characters that cannot be duplicated among terrestrial basalts.

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DISCUSSION

RADIAL DIFFUSION AND CHEMICAL STABILITY IN THE GRAVITATIONAL FIELD: A DISCUSSION[1]

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The interesting paper by Mr. Ramberg which appeared in the September, 1948, issue of this *Journal* contains several statements which may require further elaboration because they might lead geologists who are unaware of certain thermodynamic principles into erroneous conclusions. I have in mind particularly the effect of pressure on the stability of hydrous minerals (p. 455). While discussing the stability of minerals in a gravitational field, Mr. Ramberg should perhaps have pointed out, as is well known (Guggenheim, 1933), that chemical equilibrium is independent of position in such a field. If a system is in a given state of equilibrium in a closed container, this equilibrium remains unchanged whether the container is lifted 100 miles in the air or is lowered to the center of the earth, provided that the pressure in the container remains constant. When rock masses change position in the earth, the pressure acting on them does not usually remain constant but varies according to the hydrostatic law; it is this change in pressure which is responsible for such shifts of equilibrium as may result from the change in position. The effects of these changes in pressure are the same as those of any other change in pressure. In particular, the shifts of equilibrium resulting from an increase in depth must be such as would result in a decrease in the total volume of the system.

Thus, if we consider a reaction of the type

$$A \rightarrow B + H_2O ,$$

where A is a hydrous mineral and B an anhydrous one (or several), an increase in pressure will result in the formation of B at the expense of A only if the sum of the molar volumes of B and water is less than that of A. The increase in pressure, dP, required to start the reaction as written must be such that

$$|\Delta V dP| \geqslant |\Delta G| ,$$

where ΔV is the change in volume resulting from the reaction and ΔG is the free energy of formation of A from B and water at the reference pressure. Because the molar volume of water is sensitive to changes in P and T, no general statement can be made concerning the magnitude of the pressure increase required to start the dehydration reaction; in some cases this increase might be greater than the pressures encountered at the depths where metamorphic rocks are formed. Mr. Ramberg's statement that "high temperature is not necessary for the formation of the anhydrous minerals of the granulite facies" is perhaps correct under certain circumstances; it cannot be so under conditions in which the molar volume of water is large, for in such a case the effect of pressure alone would be toward the formation of the hydrous mineral at the expense of the anhydrous one.

In the same manner the "squeezing-out" of large ions by pressure may occur only if these ions, after they have been squeezed out, go into some form of lesser volume. Mr. Ramberg apparently takes the view that they move out of the system, so that their volume is not to be taken into account at all. This could happen if the squeezed crystal could evaporate into a vacuum or a medium of very low pressure, a case which is probably not encountered commonly in the depths of the earth. The squeezing-out mechanism may work in some cas es; it may not work under different conditions. In each case it should be clearly specified what the conditions of pressure and temperature are assumed to be; and also the form under which the squeezed-out ions are supposed to leave the original lattice should be stated, so that the volume relations can be worked out. But even if the volume relations are right, the minimum pressure required to start the squeezing will still depend on the energy with which the ions are held in their original lattice and may in some cases be greater than the pressures encountered under terrestrial conditions.

[1] Manuscript received October 13, 1948.

The statement concerning wollastonite at the top of page 456 may perhaps also require clarification. The present writer is not sure that he understands what is meant by "at ideal gravitational stable conditions"; but he gathers from the context that Mr. Ramberg has in view the case of a vertical column of density ρ, in which the pressure increases with depth h as $dP_1 = \rho g dh$, in contact with a column of CO_2 in which the pressure increases as $dP_2 = \rho_{CO_2} g dh$. If both columns are at the same uniform temperature and if the pressure of CO_2 at the top of the column is such that equilibrium exists there with regard to the reaction

$$CaCO_3 + SiO_2 \rightleftharpoons CaSiO_3 + CO_2 ,$$

then the equilibrium will be displaced at the bottom of the column toward the formation of wollastonite only if

$$(v_{CaCO_3} + v_{SiO_2}) dP_1 > v_{CaSiO_3} dP_1 + v_{CO_2} dP_2 ,$$

where v stands for molar volume. Substituting numerical values, we find that ρ must be greater than 2.24 gm/cm³, or, in other words, the calcite–quartz-bearing rock must have a density greater than 2.24, which will usually be the case. But in the usual case, also, the increase in pressure on the CO_2 will be the same as that on the minerals; wollastonite would then form at the bottom of the column only if the density of CO_2 exceeded 2.24 gm/cm³. Thus, at least near the surface, the equilibrium would be displaced at depth toward the formation of calcite, as usually stated.

There are a few other points in Mr. Ramberg's paper to which one might take exception, from a thermodynamic point of view, for example, his synonymous use of the words "equilibrium" and "stability." The statement in the second paragraph at the top of page 450 appears ambiguous to the present writer: surely, Mr. Ramberg does not believe, as he appears to do, that the relation between chemical potential and vapor pressure, which is really in the nature of a definition, changes with position in the gravitational field. It is, of course, precisely because the chemical potential changes with position in a gravitational field that equilibrium can be maintained only by compensating pressure and concentration gradients. The matter is clearly presented by Guggenheim (1933, pp. 153-159). The reader will find there, in a more rigorous form, the equations which Mr. Ramberg derives for the changes in composition in a binary ideal solution. Also, we surely did not have to wait for Mr. Ramberg's "proof that mechanical instability in the gravitational field results in chemical or thermodynamic instability"; the whole matter was dealt with adequately by Gibbs seventy years ago.

The above discussion should not detract from the merits of Mr. Ramberg's contribution. The present writer's purpose is mainly to emphasize how difficult it is to word a statement that will remain correct under all circumstances, although it may be correct under certain specified conditions. Because most petrologists are not in a position to follow the intricacies of thermodynamics, it should be pointed out to them that there is usually more than one side to a question. More specifically, the conditions under which a statement is believed to be true should be carefully stated, in order to avoid unwarranted extrapolations.

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RADIAL DIFFUSION AND CHEMICAL STABILITY IN THE GRAVITATIONAL FIELD: A REPLY[1]

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Everyone must agree with Mr. Verhoogen that a change of position in the gravitational field does not displace chemical equilibrium in a system closed in an impermeable container. It is equally obvious—as Mr. Verhoogen discusses at length—that if such a closed system is moved up and down in the earth, then pressure is the only variable which can displace chemical equilibrium within the system (assuming a constant temperature). The effect of pressure upon chemical equilibria in closed systems is adequately expressed by Clapeyron's equation (so commonly cited in textbooks on petrology).

These facts are, however, irrelevant to a discussion of my paper on chemical stability in the gravitational field, which necessarily implies changes of bulk chemical composition at different depths in the earth. In other words, only rocks of certain compositions are theoretically stable at given depths. In order to determine this theoretical relationship between depth and bulk chemical composition, one must assume that the rocks are more or less open systems.

By introducing the concept of a small closed system, which is moved up and down in the crust, the crucial points in my article cannot be discussed at all because the chemical communication between the system and its surroundings is artificially hindered by a completely impermeable box.

By "open system" I do not mean that the rocks necessarily are porous and full of fissures. The term should indicate only that substances are able to migrate between the system (rock) and its surroundings.

In order that a certain type of particle (atoms, ions, or molecules) may diffuse out of a rock under high pressure, it is not necessary that the rock be surrounded by a "vacuum or other medium of low pressure." The necessary thermodynamic requirement for diffusion in a certain direction is that there exists a gradient in the partial chemical potential in the same direction. The chemical potential, for example, may be high at low mechanical pressure and low at high pressure, and it follows that diffusion in such a case will be from low to high mechanical pressure. For this reason water molecules diffuse from low to high pressure in osmotic systems. Large porphyroblasts can grow in rocks under high confining pressure for the same reason.

It is well known that the thermodynamically stable state of a system is independent of the ways and velocities of reaction and can be calculated without knowledge of the kinetics of the processes. Likewise, the spontaneous reactions taking place in an unstable system tend to achieve the stable state. It may thus be worth while to try to consider the whole earth—or at least larger parts of it—as enormous and complicated physicochemical systems in which there exist instabilities of different kinds. The processes that we observe tend to change the earth as a whole into more stable states, although it is very unlikely that complete thermodynamic stability will ever be reached (C. J. Sullivan [1948] has recently published an interesting paper in which similar views are applied to granitization and ore formation).

The mechanical instabilities may be reduced by mechanical readjustment or bodily motion of matter. The chemical instabilities will usually be reduced by chemical processes only. Adjustment of large-scale chemical instabilities requires, therefore, chemical processes which are identical with long-distance diffusion.

Two questions arise: Do large-scale chemical instabilities exist in the earth? If so, does adjustment of these instabilities take place? A positive answer on these questions implies that large-scale diffusion is of geological importance. A negative answer on the second question simply means that geologists need not concern themselves with large-scale diffusion at all.

In the article discussed by Mr. Verhoogen I did not aim to point out all the large-scale chemical instabilities which exist in the earth or to show what the completely stable state of the earth should be. My aim was merely to show how gravity alone affects chemical stability in the globe. I am well aware of the fact that the effect of gravity is commonly overshadowed by the effects of other factors, such as differences of pressure or temperature or intermingling of chemically incompatible rocks. On the other hand, only by complete knowledge of the process

[1] Manuscript received October 25, 1948.

of gravitative chemical differentiation shall we be able to assign to this particular phenomenon its proper place in the whole geological picture. Therefore, considerations of the chemical processes taking place within small impermeable boxes moved up and down in the crust do not seem to be very fruitful in the solution of these questions. In one example Mr. Verhoogen touches the problem of large-scale chemical stability in the gravitational field: He notes that wollastonite tends to form at the bottom of a quartz-calcite column if the density of the column is more than 2.24 gm/cm³. In this case, where Mr. Verhoogen considers the same general phenomenon as I, some agreement is obtained. As soon as Mr. Verhoogen closes his system, however, thus abandoning the problem under discussion, his obvious conclusion is that wollastonite will not form at great depths because CO_2 is jailed in the artificial impermeable box.

One would expect to find some statements about temperature and height of the column which Mr. Verhoogen has in mind. One would also expect to find an explanation of the appearance of the somewhat mysterious value 2.24 gm/cm³. According to thermodynamics, the requirement for stabilization of wollastonite at the bottom of the column should be that the density of the quartz-calcite rock is less than about 2.90 gm/cm³, which is the density of wollastonite.

The reaction which takes place is of the following type:

$$\begin{matrix} \text{low } T & T_u & \text{high } T \\ A & \rightleftharpoons & B + C \end{matrix}, \qquad (1)$$

where A and B are solids and C is solid, liquid, or gas. If $s_B > s_A > s_C$ (where s_A, s_B, etc., are the densities of the several phases), then a thick layer of A is unstable in the gravitational field even if the temperature is below T_u. A more stable state will exist if the reaction is displaced toward B and C below a certain depth, Y, so that the dense phase, B, is formed here, while the liberated phase, C, is displaced to the top of the A layer.

At stable conditions there is a certain interrelation between the thickness, Y, of the stable A layer and the existing temperature. At temperature T_u, Y is obviously zero; and the lower the temperature, the greater the thickness Y.

At the depth Y we have

$$dF_A = -S_A dT + V_A dP\,, \qquad (2)$$

$$dF_B = -S_B dT + V_B dP\,, \qquad (3)$$

$$dF_C = -S_C dT + M_C dY\,, \qquad (4)$$

where F_A, F_B, etc., are the molal free energies of the several phases; S_A, S_B, etc., are the entropies of the phases; V_A and V_B are the molal volumes of the phases A and B; M_C is the molecular weight of C; and P is pressure at depth Y.

The conditions for equilibrium between A and B at depth Y and C on the top of the A layer are

$$dF_A = dF_B + dF_C\,. \qquad (5)$$

Introducing $dP = s_A dY$, and $S_B + S_C - S_A = Q/T_u$ in equation (5) gives

$$\frac{dT}{dY} = \frac{V_B s_A + M_C - M_A}{Q} \cdot T_u\,, \qquad (6)$$

which is the relation between temperature, T, and thickness, Y, of the stable A layer situated between B and C.

The reaction $A \rightarrow B + C$ is endothermic, so that Q is positive. The requirement for gravitative splitting-up of A at temperatures below T_u is that dT/dY be negative, i.e., that $(V_B s_A + M_C) < M_A$. This condition is satisfied if $s_A < s_B$, since in this case $s_A V_B < M_B$ and $M_B + M_C$ certainly always equals M_A.

If the liberated C phase remains at the depth Y instead of being elevated, the term $M_C dY$ in equation (4) changes into $V_C dP$ or $V_C s_A dY$, and equation (6) is identical with Clapeyron's equation. It follows that if $s_A > s_C$, then $V_C s_A dY > M_C dY$, and the free energy of the system will be less if C is elevated to the top than if it remains at depth Y.

Consequently, as stated in my article, the requirement for gravitative chemical differentiation in the system $A \rightleftarrows B + C$ is that $s_B > s_A > s_C$, combined with a minimum thickness of the original A layer.

Let us take dehydration of gypsum as a simple example:

$$CaSO_4 \cdot 2H_2O \overset{T_u}{\rightleftarrows} CaSO_4 + 2H_2O\,.$$

Heat of dehydration is about 4.7 cal. and $s_{gyp} = 2.96$ gm/cm³, $s_{anh} = 2.32$ gm/cm³, $T_u =$

436°,[2] which can be introduced into equation (6); hence

$$dT/dV \cong -0.007 \text{ degrees/meters}.$$

For example, at 366° K a gypsum layer in the uppermost parts of the earth is unstable, provided that it is more than 10 km. thick. Below this depth anhydrite will tend to form, and the liberated water molecules tend to migrate toward the top. At a depth of about 30 km. the same process tends to take place at as low a temperature as 226° K.

Let us give briefly the reaction between muscovite and phlogopite in which garnet and potash feldspar are formed:

$$\underset{\text{phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{quartz}}{3SiO_2} \overset{\text{low } P\text{–}T}{\rightleftharpoons} \underset{\text{pyrope}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{potash feldspar}}{2KAlSi_3O_8} + 2H_2O\,. \tag{7}$$

The left side corresponds to A of equation (1), pyrope to B, and potash feldspar plus water to C. The density of pyrope is 3.51 gm/cm³, that of muscovite about 2.8 gm/cm³, and that of phlogopite also about 2.8 gm/cm³.

In this case the quantity $V_{B^5A} + M_C - M_A$ equals about -82 gm, whereas the same quantity in the case of gypsum is about -30 gm. If the heat of transformation were known, it would be possible, at every temperature below T_u to determine the depth at which pyrope tends to form at the same time that potash feldspar and water tend to gather on the top of an idealized thick muscovite-phlogopite layer.

Mr. Verhoogen's emphatic statement that the relation between chemical potential and vapor pressure is constant by definition, regardless of the position in the gravitational field, is untenable; for the vapor pressure is independent of position in the gravitational field but the chemical potential changes according to the following formula: $d\mu/dV = M$, where M is the molecular weight of the component considered. It is obviously the "constant" K which changes in equation $\mu = RT ln\pi + K$.

[2] These data are taken from Handbook of Chemistry and Physics, ed. 30, Chem. Rubber Pub. Co., Cleveland, 1947.

REFERENCES CITED

RAMBERG, HANS (1948) Radial diffusion and chemical stability in the gravitational field: Jour. Geology, vol. 56, pp. 448–458.

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REVIEWS

"The Geological Approach to the Study of Soils." By W. H. BRYAN. (Presidential Address: Section C, Geology.) (*Report of the 25th Meeting of the Australian and New Zealand Association for the Advancement of Science*, 1946.) Adelaide, 1948. Pp. 52–69.

Professor Bryan's thesis is that soil study is a necessary part of a geologist's equipment; for not only does the terrain affect the soil, but soils are themselves important geological units either as markers of epochs in stratigraphical geology or as controls of geomorphic processes.

The heads under which the thesis is developed are "Soils as Seen from Below," "Soils and Past Climates," "Influence of Landscape on Development of Soils," "Influence of Soils on Development of Landscape," and "Soils as Stratigraphical Aids."

Bryan agrees that "extensive superficial deposits may be regarded as geological formations and used in a strictly stratigraphical sense," a dictum based on Woolnough's claim that the "duricrust" of Australia—a relict layer originating from a widely developed ancient soil truncated by wind—must rank as a "stratigraphical unit"; and he stresses also the value for Pleistocene subdivision of the alternation of soils with loess formations in Nebraska and elsewhere.

Under the head "Influence of Landscape on Development of Soils" he makes the point that

> study of inherited soils found on residuals of earlier landscapes [might help] to answer the vexed question as to which, if any, of the higher remnants are truly residual surfaces. . . . All those flat-topped areas that carry a well-matured, deep soil may be confidently assigned to the original surface. . . . By combining the disciplines of geomorphology and pedology and using only those residuals that satisfy the criteria of both, there may be achieved a . . . reconstruction of the original peneplain surface. . . . Where the physiographic evidence suggests that there are present the remnants of two peneplains in the same area, a comparison of the soils of the two groups of residuals may be used to test the suggestion. . . . Yet another step . . . may be taken by the use of soils in the recognition and correlation of coeval peneplains in widely separated areas.

Examination of the "Influence of Soils on the Development of Landscape" leads to the "startling" suggestion that in the course of the normal geographic cycle, the development of characteristic and contrasting types of landscape profile is strongly influenced by soil type; for "some soils in their natural state are almost proof against erosion," while others not only facilitate runoff and sheet erosion but also are subject themselves to mass movement, soil creep, and solifluction.

> Let us examine the probable effects of two widely different soil types on the subsequent cycles of erosion. A suitable choice for our purpose would seem to be a strongly pedalferric soil such as a lateritic red earth and, for contrast, a typically pedocalcic soil such as a black earth. . . . The physical properties of such red earths as occur on small plateau remnants in southeastern Queensland are of a striking kind. The soils consist largely of an assemblage of clay minerals of low silica-alumina ratio, and consequently are remarkably friable and show little expansion on wetting. Further, the aggregation of the clay particles is such that the soil is very porous, with an internal drainage almost as free as that of loose sand. Such friable, porous clay soils are remarkably resistant to erosion—indeed they are almost erosion-proof. . . . Such soils are so absorbent that even heavy rainfall produces very little surface run-off. . . . This combination of properties provides a very effective protection for the rock beneath. . . . In such circumstances the erosive forces acting upon our uplifted peneplain will be concentrated in and restricted to a small number of very widely spaced streams fed almost entirely by ground water, in each of which vertical corrasion will be far more effective than lateral erosion. The characteristic plateau topography thus developed early in the cycle will be reflected right through to the end. . . . Residuals . . . will remain steep-sided, flat-topped, and soil-protected to the end. . . .
>
> In vivid contrast to such a picture is that to be deduced when the original soil cover of the uplifted peneplain is of a strongly pedocalcic nature such as a black earth. . . . This black soil too consists largely of clay, but this clay is made up of minerals of a high silica-alumina ratio, and is notoriously adhesive and tenacious. It expands greatly on wetting, is very easily eroded, and, on even moderate slopes, is very subject to landslides. The effect of rain is quickly to saturate the upper part of the soil, thus forming a sodden, impervious mass over which the excess water flows . . . carrying with it considerable quantities of soil, the result of natural sheet erosion. The civil en-

gineer detests these black soils, which are as dynamic as the red earths are static. . . .

The picture that we now observe is in sharp contrast with that due to the protecting influence of the red earths. Far from acting as a protective cover of the original surface, the black earths will tend to move laterally into valley depressions as soon as the valley sides are sufficiently inclined to permit movement down their slopes. As a result of the continuous migration of soil from the intervening ridges the rocks beneath these are recurrently exposed to provide more soil, further to feed the valleys and thus perpetuate the original landscape pattern at progressively lower levels. From the very beginning the landscape takes on an "old" appearance, which it retains through youth and maturity until it becomes old in fact as well as in appearance. Throughout the whole cycle the "rolling downs" motif is manifest. "Black-soil plains," as they are called, are similar in many parts of the world, and all conform to one geomorphic type in spite of the fact that they must represent different stages in the cycle of erosion. Consequently such areas give no clue as to the position of the original peneplain from which their present surfaces were derived. Whereas the landscape developed under the red earths jealously preserves the proof of its origin, that covered by the black earths automatically effaces the evidences of its own history.

C. A. COTTON

Sequence in Layered Rocks. By ROBERT R. SHROCK. New York: McGraw-Hill Book Co., Inc., 1948. Pp. 507; figs. 397. $7.50.

The author's purpose is to "describe and illustrate top and bottom features in all kinds of bedded and layered rocks." It is surprising, at first thought, that this topic could be the subject of a 507-page book. A wide range of material has been consolidated into an almost complete compendium of what is known about one of the most fundamental concepts of geology—superposition.

The book is descriptive and extremely well done. A total of 397 sketches and photographs evidences the care taken in the preparation of topics. Abundant quotations from published papers and numerous personal communications are included. Complete references to quoted material facilitate further inquiry into a particular subject. It is regrettable that the extensive non-English literature has not been consulted in the preparation of the book.

The completeness of the work would have been tremendously enhanced if the author had included such allied subjects as sedimentation rates, the problem of geologic time, evaluation of geophysical well logging in determining sequence, and a fundamental discussion of time, lithologic, and fauna surfaces.

N. A. R.

Chambers's Mineralogical Dictionary. Brooklyn: Chemical Publishing, Inc., 1948. Pp. 47; colored pls. 40. $4.75.

This booklet consists primarily of an alphabetical listing of minerals, rocks, and structures. Some fourteen hundred items appear in fine print. The definitions given are popular and of no value to the serious student of the subject. The only illustrations are very mediocre color plates. These are indexed.

D. J. F.

ERRATA

In "The Unique Association of Thallium and Rubidium in Minerals," by L. H. Ahrens, in the November, 1948, *Journal:*

P. 578, col. 1, line 13, *read* PbS *instead of* Pbs.

P. 579, col. 1, line 20, *read* Cs^+ *instead of* Cs.

P. 580, col. 2, line 3, *read* Rb_2O/Tl_2O *instead of* RB_2O/Tl_2O.

P. 585, col. 1, line 6, read $x = 0$ instead of $x = O$.

P. 587, col. 2, line 1, *read* "alkali-metal" *instead of* alkali-metal.

P. 588, table 4, col. 3, line 10, *read* 0.00031 *instead of* 0.0031.

P. 590, col. 1, line 6, *read* "alkali-metal" *instead of* alkali-metal.

COMMUNICATIONS AND ANNOUNCEMENTS

NATIONAL RESEARCH COUNCIL COMMITTEE ON THE INTERRELATIONS OF PLEISTOCENE RESEARCH

A broad understanding of earth conditions during the Pleistocene has become necessary in fields of scientific endeavor other than those of geology and prehistoric archeology. In studies as diverse as pedology, climatology, biology, and oceanography, productive research effort requires considerable knowledge of progress made in the related fields of Pleistocene investigation. As a means of promoting fruitful contacts among workers in these several sciences, the National Research Council established in June, 1947, a Committee on the Interrelations of Pleistocene Research under the chairmanship of Professor Richard Foster Flint, of Yale University. Working with the chairman are the following: Edward S. Deevy, Jr. (biogeography), Department of Biology, Yale University; Loren D. Eisley (anthropology and New World archeology), Department of Anthropology, University of Pennsylvania; Claude W. Hibbard (vertebrate paleontology), Museum of Paleontology, University of Michigan; Chauncey D. Holmes (glacial erosion and sedimentation), Department of Geology, University of Missouri; Helmut E. Landsberg (meteorology and climatology), Committee on Geophysical Sciences, Research and Development Board, Washington, D.C.; Hallam L. Movius, Jr. (Old World archeology), Peabody Museum of Archeology and Ethnology, Harvard University; Fred B. Phleger, Jr. (oceanography and sea-floor geology), Department of Geology, Amherst College; Louis L. Ray (glacial stratigraphy; alpine glacial geology), United States Geological Survey, Washington, D.C.; H. T. U. Smith (eolian features; frozen ground; stream terraces), Department of Geology, University of Kansas; and James Thorp (soil science), Division of Soil Survey, United States Department of Agriculture, Lincoln, Nebraska.

Preliminary reports were circulated among the membership, and on April 5 and 6 the committee held its first meeting. The results are most encouraging. To make its work as effective as possible, the committee welcomes correspondence with scientists in any field in which the combined resources of the committee can be of assistance. Such correspondence should be directed to the individual member representing the particular field, or to the chairman.

CHAUNCEY D. HOLMES

DEPARTMENT OF GEOLOGY
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COLUMBIA, MISSOURI

SYMPOSIUM ON MINERAL RESOURCES

The Department of Geology and Geography of the University of Tennessee is sponsoring a symposium on the mineral resources of the Southeast. Sessions will be held on the campus at Knoxville on March 3, 4, and 5. Papers on the major metallic and nonmetallic mineral products of the Southeast will be presented by invited speakers.